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# SULFIDE PRODUCTION IN WASTE STABILIZATION PONDS

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# SULFIDE PRODUCTION IN WASTE STABILIZATION PONDS

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## ABSTRACT

This investigation deals with the production and release of hydrogen sulfide from waste stabilization ponds. All experiments were conducted under controlled environmental conditions using laboratory models.

A 6-foot deep model facultative pond was studied under seven different operating conditions. The experiments were designed to evaluate the relationships between sulfide concentration in the pond and four operating characteristics, namely: detention, concentration of sulfate ion in the influent, BOD surface load and sulfate ion concentration in terms of surface load.

At constant detention time and BOD surface load a linear relationship was found to apply between sulfide concentration in the pond and sulfate concentration in the influent.

Increases in sulfide concentrations in the pond from zero to about 1 and 2 mg/l, respectively, were accompanied with drops in oxidation-reduction potentials of about 80 and 120 mv; further increases in sulfide concentration affected the ORP in a lesser way.

Sulfide concentrations in the pond of about 7 mg/l were accompanied by an almost complete disappearance of algae, but the BOD removal rates were not affected appreciably.

Infrared spectroscopy was used to study the gaseous emissions from the pond. However, the interference of moisture in the air samples limited the identification to only three gases, namely: methane, hydrogen sulfide and carbon dioxide.

An appraisal was made of the engineering design applications of the results of the investigation, as well as some suggestions for future research.

## CONCLUSIONS

1. The average sulfide concentration in a stabilization pond, $[S^{=}]$, can be estimated by an expression as follows:

$$[S^{=}] = K[SO_4^{=}]$$

where $[SO_4^{=}]$ is the concentration of sulfate ion in the influent. The dimensionless constant, K, is a function of the operating characteristics and the average temperature of the pond.

2. For a 6-foot deep facultative pond the following empirical relationship was found to give fair estimates of the constant, K:

$$K = a[\text{BOD surface load}] + b[\text{detention time}] + c$$

For an average pond temperature of 25°C, the following values of the coefficients were determined:

$$a = 0.0001185$$

$$b = -0.001655$$

$$c = 0.0553$$

3. Two empirical equations were developed to estimate sulfide concentration in a pond:

$$[S^{=}] = a[\text{BOD surface load}] + b[SO_4^{=}]\ \text{influent concentration} + c[\text{detention time}] + d$$

$$[S^{=}] = a'[\text{BOD surface load}] + b'[SO_4^{=} \text{ surface load}] + c'[\text{Detention time}] + d'$$

The coefficients a, b, c, d, a', b', c', and d' were computed for various operating conditions.

4. Under these test conditions the sulfide concentration was reduced 5 to 25% during the day as compared to the dark periods. This reduction in concentration occured as a result of the oxidation of sulfide by the photosynthetic oxygen.

5. The average sulfide concentration over a 24-hour period, in the top 40 cm of the test pond was about 40% to 90% of the average sulfide concentration throughout the pond.

6. Algae virtually disappeared when the sulfide concentration reached 6 to 7 mg/l; yet a sulfide concentration of 8 mg/l did not seem to affect the BOD removal rates.

7. Increases in sulfide concentration from near zero to near 1 and 2 mg/l, respectively, reduced the oxidation-reduction potential 80 and 120 mv. Further increases in sulfide concentration reduced the ORP in lesser amounts. These results support the use of ORP measurements to detect potential problems arising from sulfide odors.

8. The rate of transfer of hydrogen sulfide from water to the atmosphere can be expressed by a Fickian relationship

$$q = k(c - c_{eq})$$

At 22°C, under quiescent conditions the value of k was found to be about 0.006 m/hr. Wind and wave effects on the water surface will increase k.

9. The oxygen diffused from the atmosphere into the water seems to be readily reduced by the escaping hydrogen sulfide in the water surface film. Odor problems will occur when the rate of hydrogen sulfide oxidation in the surface film is not large enough to prevent the escape of hydrogen sulfide.

10. Exchanges of methane, carbon dioxide and hydrogen sulfide between the laboratory pond and the atmosphere were detected by infrared spectroscopy. The procedure used seems to be particularly suited for the study of gaseous emissions from ponds.

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Chapter 1

# INTRODUCTION

This investigation was directed to the study of the production and release of hydrogen sulfide in waste stabilization ponds. All the experiments were conducted in laboratory models under controlled environmental conditions.

The occurrence of sulfide in a pond was studied in a relation to four operating conditions; namely, BOD surface load, concentration of sulfate ion in the influent, detention time, and sulfate surface load. The experiments were conducted in a 6-foot deep model facultative pond. The model was operated under seven different operating conditions. The operating characteristics of the seven tests were designed to enable development of empirical relations between sulfide concentrations in the pond and the four parameters mentioned. This part of the investigation included an evaluation of the relations between sulfide concentration in the pond and oxidation-reduction potentials, inhibition of algal activities, and efficiency of the model in the removal of BOD.

The exchange of gases between the pond model and an enclosed volume of air in contact with the pond was studied by infrared spectroscopy. The interference of moisture in the air samples limited the study to only three gases: methane, hydrogen sulfide, and carbon dioxide.

Quantitative determinations were made of the hydrogen sulfide released by the pond during 12, 24, and 48 hr. periods. The determinations were made for the model working under different operating conditions, but in all cases no escape of hydrogen sulfide could be detected with the procedure used. The possibility that these results are a model, but not a prototype, characteristic is discussed after consideration of the results obtained in the experiments described in the next paragraph.

Considering that the environmental problems occur as a consequence of the hydrogen sulfide released by the pond, a complementary set of experiments was undertaken to determine the rate of diffusion of hydrogen sulfide from water under different conditions. This study included an evaluation of the importance of surface reaeration in the oxidation of dissolved sulfides.

In the last chapter is presented a discussion of the engineering design applications of the results of this investigation and some suggestions for future research in the problems of odors from ponds.

Many years of field practice have established stabilization ponds as a low cost and reliable method of waste treatment. In 1962, 2474 stabilization ponds were reported in operation in the United States (56), 1647 treating domestic sewage and 827 industrial wastes. In Texas the figures were 279 municipal ponds (as compared with 188 reported in 1957 (49)) and 19 industrial ponds.

The three factors that have most influenced the acceptance of stabilization ponds as a waste treatment system seem to be:

First, the efficiency of stabilization ponds in the degradation of organic materials. This topic has been treated in the literature by various authors (17, 22, 38, 40, 48, 49).

Second, health hazard considerations. Coetzee et al(12) studied the removal of pathogenic bacteria in waste stabilization ponds and concluded that stabilization ponds offer "a safer barrier against disease than conventional methods of sewage purification." Higgins (25), commenting on a controversial article on stabilization ponds that appeared in the Journal of the Canadian Medical Association (41), points out that even if much research is needed on the subject, there are not, at the present, grounds for discontinuing the use and development of waste stabilization ponds. At the present time the general concensus seems to be that, when properly designed and operated, waste stabilization ponds do not represent a health hazard.

Third, odor problems. The lack of a sound basis to estimate the potential odor problems has probably been the main reason for limiting the use of waste stabilization ponds. The chemical compounds most often associated with odors from ponds include: sulfides and mercaptans, also amines and polyamines produced during bacterial decomposition of proteins, e.g., putrescine and cadaverine, (tetra- and penta-methylene diamine, respectively). Also produced in the

decomposition of protein are indole (2-benzopyrrole), and skatole (3-methyl indole). Other odorous compounds produced in ponds are the metabolic by-products of actinomycetes, e.g. ketones, aldehydes, saturated fatty acids, and unsaturated aromatics (43).

Stabilization of wastes is achieved in a pond by a unique algal bacterial process. The aerobic oxidation that takes place in the upper part of the pond is combined with the anaerobic oxidation of organics occurring in the bottom of the pond. The aerobic conditions in the upper part are maintained by surface reaeration and photosynthetic oxygenation. This oxygenated upper layer serves as a protective shield in keeping the odorous end products from escaping. Under an oxygenated environment, gaseous odorous materials are chemically or biochemically oxidized and rendered innocuous before they reach the surface.

During periods of upset, however, photosynthetic oxygenation may be inhibited and some odorous compounds may reach the atmosphere, and as a consequence, serious odor problems may result. It should be noted that odors in ponds can also have a different origin, viz., the end products of the metabolism of certain blue-green algae, diatoms, pigmented flagellates, and the products released by dead algal cells.

The causes of upset and mechanisms of photosynthetic oxygenation are outside the scope of this investigation; information on this aspect can be found in some recent studies (26, 31, 69).

The most important sulfide source in a pond is the biological activities of the sulfate-reducing bacteria. The first investigation on the sulfate-reducing bacteria dates back to the now classical studies made by Beijerinck in 1895 in Holland (68, p607). In sanitary engineering the sulfate-reducing bacteria have been studied in relation to corrosion problems in pipe lines (34) and odor problems in sewer lines and sewage plants.

Chapter 2

# LITERATURE REVIEW AND ANALYSIS OF THE PROBLEM

The literature review is divided into three sections. The first section deals with the microbiological aspects of sulfur transformations in nature. The second section deals with the occurrence of these transformations in waste stabilization ponds, and the third section discusses the physical-chemical aspects of the equilibrium and transfer of gases from water to the atmosphere. Special emphasis is directed to the water-hydrogen sulfide system.

Along with the literature review brief analysis are made of some basic concepts that are used in the interpretation and discussion of results.

## 2.1 - Microbiological Sulfur Transformations

The transformations that sulfur undergoes in nature may be envisaged as a closed cycle, similar, if less complex, to the well known nitrogen cycle. In the study of the sulfur cycle, Fig. 2.1, account must be made of the sulfur that is incorporated into the cycle from geochemical sources. The two most important geochemical sources (27, p 753) are: (a) $CaSO_4$ that is present in some sedimentary rocks and is moderately soluble in water, and (b) sulfate that is derived from the oxidation of sedimentary pyrite:

$$4\,FeS_2 + 15\,O_2 + 2\,H_2O \longrightarrow 2\,Fe_2(SO_4)_3 + 2\,H_2SO_4 \qquad (2.1)$$

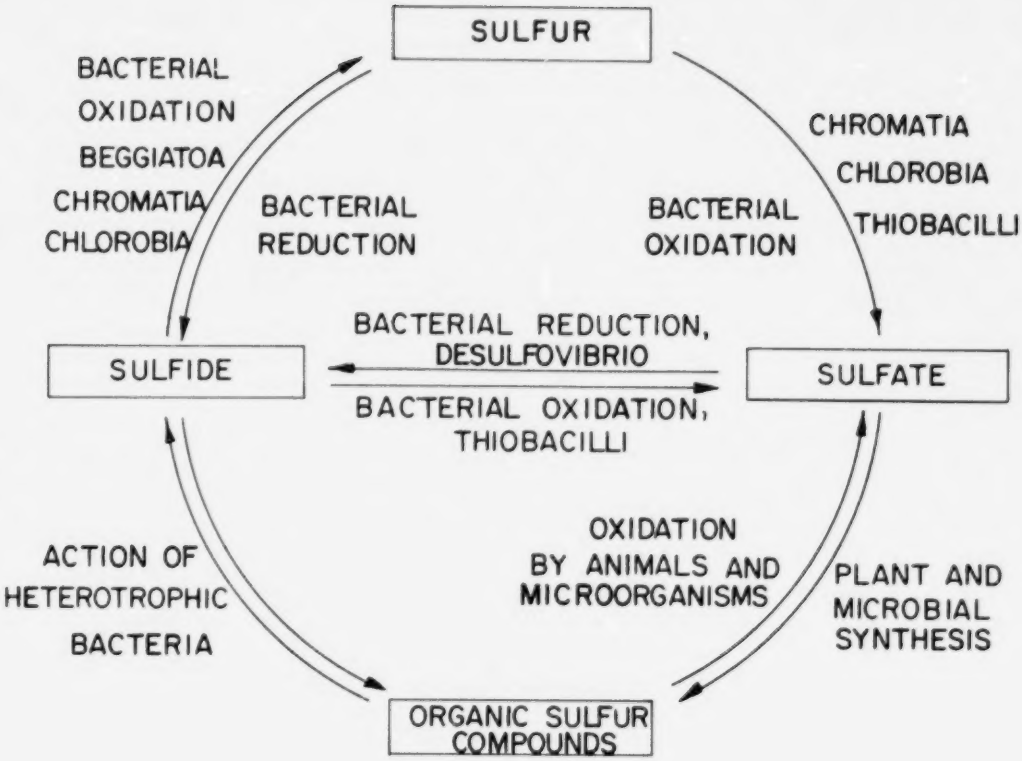



FIG. 2.1.- MICROBIOLOGICAL TRANSFORMATIONS OF SULFUR

These two natural sources probably account for the high concentration of sulfates sometimes found in fresh water. Sulfate is usually the second or third most abundant ion present in water. This anion is exceeded only by bicarbonates and in some cases by silicates.

The microbiological transformations of sulfur compounds have been described by several authors (8, 19, 59, 65, 74). For the purposes of this investigation, it has been considered convenient to summarize the most important bacterial transformations according to the following scheme:

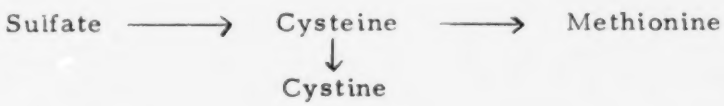
A. When the sulfur compound becomes part of the cell there is:
   1. synthesis of sulfur-containing amino acids
   2. synthesis of sulfur-containing organic cofactors

B. When the sulfur compound does not become part of the cell the sulfur compound becomes:
   1. a hydrogen acceptor
   2. a hydrogen donor and carbon dioxide and (or both) molecular oxygen becomes the hydrogen acceptors.

Reactions in group "A" would be of importance when the synthesis of these compounds is the limiting factor of bacterial activity in a pond. However, this is not the usual case.

In the living cell sulfur occurs almost exclusively in its reduced form (65 p 541). For this reason hydrogen sulfide can serve as a sulfur source. Most bacteria, as well as fungi, can also grow and

synthesize amino acids utilizing inorganic sulfate as a sulfur source (74). An example of this synthesis has been demonstrated with $^{35}SO_4^{=}$ and E. Coli (5). For most microorganisms the overall synthesis reaction is believed to be (74):

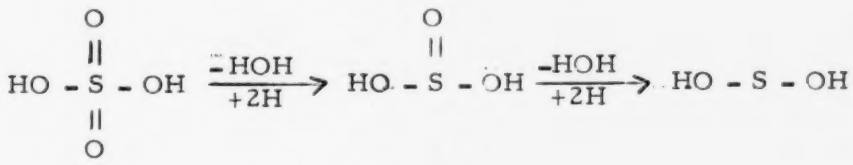



Four of the organic cofactors present in bacterial cells contain sulfur, namely: Biotin, Lipoic Acid, Pantothenic Acid, and Thiamine. Microorganisms differ markedly in their ability to synthesize these compounds (6, 13). In waste stabilization ponds these compounds are not believed to be limiting factors in bacterial activity.

The reactions of group "B" in the scheme shown before are particularly important in the study of sulfide production in stabilization ponds.

These reactions are discussed in the following paragraphs in some detail.

The Sulfur Compound as Hydrogen Acceptor: The organisms able to carry on these reactions are strict anaerobic heterotrophs. They include curved rods (such as Desulfovibrio desulfuricans) and straight rods (Clostridium nigrificans). All of these are gram-negatives (19, 42, 68). The postulated reactions of sulfate reduction are (68):



$$\xrightarrow[+2H]{-HOH} HO - S - H \xrightarrow[+2H]{-HOH} H - S - H \qquad (2.2)$$

In the Desulfovibrio system only sulfite is formed at pH 7.75; if the reaction is carried out at pH 6.0 hydrogen sulfide is formed ( ).

The overall system for the reduction of sulfate to sulfite is:

$$H_2 + \text{Cyt } C_3(2Fe^{+++}) \longrightarrow \text{Cyt } C_3(2Fe^{++}) + 2H^+$$

$$ATP^{-4} + SO_4^{-2} + H^+ \longrightarrow APS^{-2} + PP^{-3}$$

$$APS^{-2} + \text{Cyt } C_3(2Fe^{++}) \longrightarrow AMP^{-2} + \text{Cyt } C_3(2Fe^{+++}) + SO_3^{-2}$$

The above reactions can be summarized as follows:

$$H_2^+ + ATP^{-4} + SO_4^{-2} \longrightarrow AMP^{-2} + PP^{-3} + H^+ + SO_3^{-2} \qquad (2.3)$$

where:

APS - = adenosine - S - phosphosulfate

PP = pyrophosphate

AMP and ATP = adenosine mono- and tri-phosphate.

The energy released in this reaction is:

$$SO_4^{-2} + H_2 \longrightarrow SO_3^{-2} + H_2O + 14,000 \text{ Cal} \qquad (2.4)$$

A wide variety of organic compounds can serve as hydrogen donors for Desulfovibrio including: glucose, lactose and some amino acids (68).

The Sulfur Compound as Hydrogen Donor: Two markedly different types of microorganisms are able to oxidize sulfur compounds. They can be characterized according to the hydrogen acceptor used.

The first group is formed by the photosynthetic sulfur bacteria utilizing $CO_2$ as hydrogen acceptor. These bacteria are autotrophic anaerobes and require both light and sulfides. In this group are included the green Chlorobacteriaceae and the purple Thiorhodaceae.

The oxidation of hydrogen sulfide is carried in two main steps (68):

$$CO_2 + 2H_2S \xrightarrow{(light)} (CH_2O) + H_2O + 2S \qquad (2,5)$$

$$3CO_2 + 2S + 5H_2O \xrightarrow{(light)} 3(CH_2O) + 2H_2SO_4 \qquad (2,6)$$

An important feature of this photosynthetic reaction is that no molecular oxygen is formed.

The second group of bacteria able to oxidize sulfide is formed by the colorless sulfur bacteria, utilizing molecular oxygen as a hydrogen acceptor. The colorless sulfur bacteria are strict aerobes that require sulfide to grow. Since sulfide is promptly oxidized by dissolved molecular oxygen, very special environmental situations must exist for this group of bacteria to grow. Examples of such situations are the surface of sewage channels in the zones near to the walls. In these particular locations sulfide is made available from diffusion of the sulfide produced at the bottom of the channel, and oxygen is available by surface aeration. These environmental conditions are also satisfied in some sulfur springs (32).

Some authors (74) subdivide the colorless sulfur bacteria in two groups according to the form of oxidation carried on, namely:

A. The filamentous forms, including Beggiatoa alba, that oxidize sulfide to intracellular elementary sulfur:

$$H_2S + \frac{1}{2} O_2 \longrightarrow S + H_2O \qquad (2.7)$$

When the sulfide concentration in the medium decreases the intracellular sulfur is further oxidized to sulfate:

$$S + H_2O + 1\frac{1}{2} O_2 \longrightarrow H_2SO_4 \qquad (2.8)$$

The optimum sulfide concentration for Beggiatoa alba seems to be in the order of 6.25 mg/l (this value was computed based on some data given by Thiman (68 p 714.)

B. The unicellular forms, such as Thiobacillus thiooxidans, that do not contain sulfur globules.

Most of what has been said in this section has been directed to bacteriai metabolism. Before closing this section a brief discussion is presented of the role of sulfur in algal metabolism.

Most of algae forms can reduce and utilize sulfate as their sole sulfur source (33). The uptake and accumulation of sulfate by Chlorella pyrenoidosa was studied by Wedding and Black (72). Schiff (60, 61) studied the effects of light, time and external sulfate concentration in

the assimilation of sulfate by Chlorella, both of these studies were made with $^{35}S$ and it was found that sulfur was excreted mainly in its reduced form.

## 2.2 - Sulfur Transformations in Stabilization Ponds

In this section are discussed those reactions involving the oxidation or formation of sulfide in waste stabilization ponds. The presence or absence of the microorganisms able to carry on these reactions is highly dependent on various environmental conditions. Some of the most important factors influencing these special biological growths are: temperature, pH, oxidation-reduction potential, dissolved oxygen and light intensity. The values that these parameters take in a facultative pond change along the depth of the pond. Figure 2.2 shows a typical kind of stratification that may be found in a pond (17, 49). The values shown in the scale of Fig. 2.2 are given only to indicate the range of variation in values of these parameters and do not correspond to any actual determinations made.

In Fig. 2.2 three zones are marked:

A. the top layer, typical of illuminated, aerobic condition

B. the middle zone, partially illuminated and aerobic, and

C. the bottom zone, turbid and anaerobic.

The reactions to be discussed in the next paragraphs are referred to these three zones. The discussion of reactions in stratified ponds is

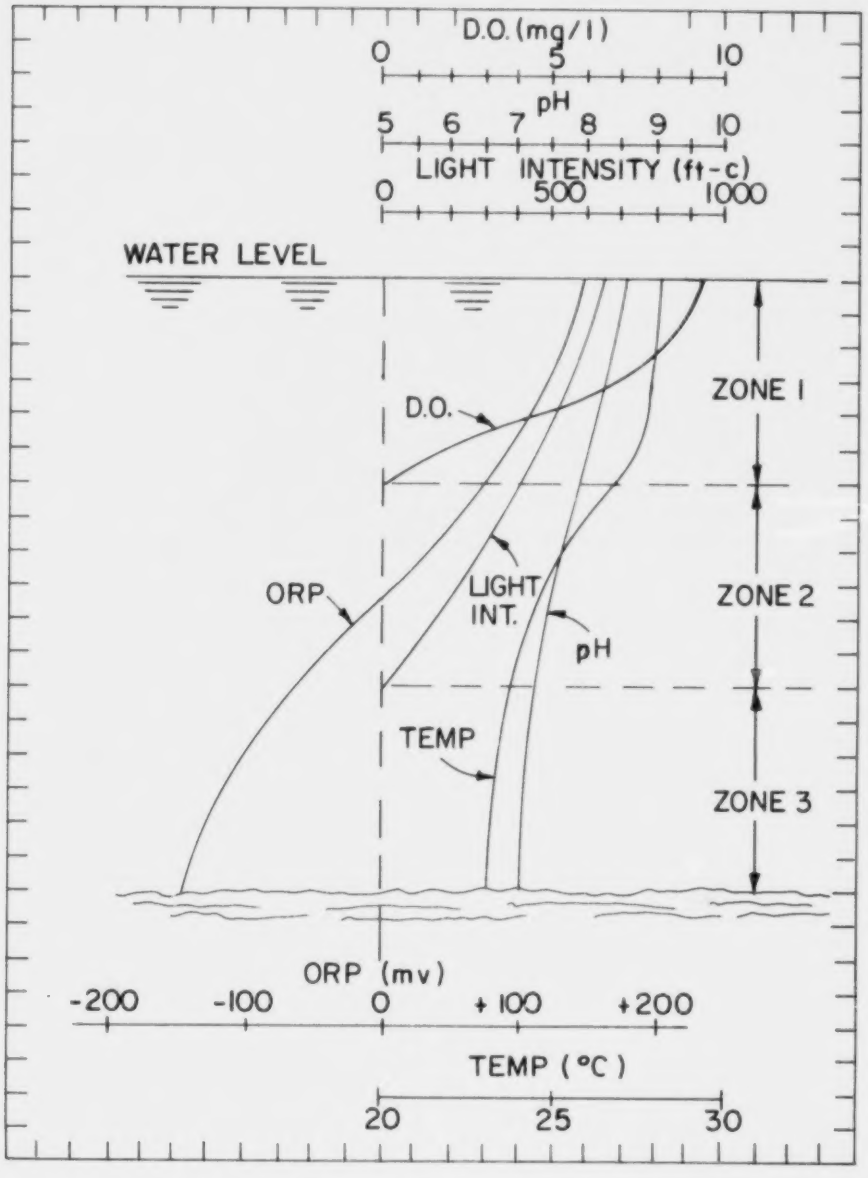



FIG. 2.2.- TYPICAL STRATIFICATION CURVES IN FACULTATIVE PONDS

divided into two sections: the first deals with sulfate reduction and the second deals with sulfide oxidation.

Sulfate Reduction: Anabolic reduction of sulfate can occur in all three zones, Fig. 2.2. In anabolic reductions of sulfate the reduced sulfur compound becomes part of the cell. These sulfur compounds are eventually released by the cell to the medium, also in a reduced form. But the amounts of sulfide formed in this manner are negligible as compared with the sulfide formed from other sources in a treatment pond.

The largest amount of sulfide produced in a pond occurs during the reduction of sulfate by those bacteria that utilize sulfate as an inorganic hydrogen acceptor in their catabolic reactions. The most characteristic specie of this group of sulfate-reducing bacteria is Desulfovibrio sp.. According to some authors (75) the optimum oxidation potential ($E_H$) for growth of sulfate reducing bacteria is between -100 mv and -300 mv at pH 7.0. No growth has been observed at potentials more positive than +27 mv (2); these two reports are cited by Wheatland (73). Results obtained by Wheatland himself in the study of the activities of the sulfate-reducing bacteria in synthetic substrate and in a polluted estuary support these ORP values. The reduction of sulfate is inhibited by the presence of any significant amount (about 0.16 mg/l) of dissolved oxygen (73).

The two mentioned environmental conditions, namely, presence of dissolved oxygen and positive oxidation reduction potentials limit the occurrence of sulfate reduction by Desulfovibrio to zones 2 and 3 of Fig. 2.2.

The inhibition of hydrogen sulfide production in sewage by dissolved oxygen and by high oxidation potentials has been a well known fact in sanitary engineering practice for many years. Reports on the prevention of sulfide formation by aeration or by addition of $NaNO_3$ go back to 1937 (23, 36). Parker et al (52) report sulfide concentration in the order of 2 to 4 mg/l in sewage lagoons when properly operated.

For sulfide concentration values above 8.4 mg/l algae disappearance in stabilization ponds has been reported (52); apparently hydrogen sulfide was the responsible toxic agent. Palmer (50) gives concentrations of hydrogen sulfide of 3.9 mg/l as toxic for most diatoms.

The rate of sulfide production is also dependent on sulfate concentration and water temperature; Ohle (47) found in lakes a linear relation between sulfide production and sulfate concentration. Results on the effects of temperature in sulfide production show a sharp decrease in bacterial formation of sulfide for temperatures below 15°C; above this temperature the rate of formation approximately doubled for each 10°C rise in temperature.

The bacterial production of sulfide under optimum environmental conditions can be considerable. It has been considered as an industrial

process for the production of hydrogen sulfide (used in the manufacture of sulfuric acid) using sewage enriched with $CaSO_4$ as a growth medium (9).

Sulfide Oxidation: The oxidation of sulfide in a pond can be carried on by colorless sulfur bacteria and by colored photosynthetic bacteria. The best environmental conditions in a pond for the growth of colorless sulfur bacteria would be the top layer of the pond, where both dissolved oxygen and hydrogen sulfide can occur. However, colorless sulfur bacteria are not often found in stabilization ponds, and when present are in rather low numbers. Therefore the oxidation of sulfide by colorless sulfur bacteria can be neglected when compared with the oxidation carried on by photosynthetic bacteria and with the oxidation of sulfides by dissolved molecular oxygen.

The photosynthetic sulfur bacteria are very often found in large numbers in stabilization ponds, particularly during the summer and fall months. When present they impart to the pond a characteristic brown or red color. The presence of photosynthetic sulfur bacteria has been reported in many different types of ponds, including: sewage ponds (51), refinery waste ponds (14) with reported concentrations of $1.4 \times 10^7$ cells/ml of Chromatium, rendering waste ponds (14) with reported concentrations of $6.17 \times 10^7$ cells/ml of Thiopedia, and also in a series of ponds in Pullman (Washington) receiving the effluent of a colony of white rats research installation (18). In all of these cases

a reduction in hydrogen sulfide odors accompanied the appearance of photosynthetic sulfur bacteria; for this reason photosynthetic sulfur bacteria are sometimes referred to in the literature as "biological deodorizer".

A comprehensive study of the activities of photosynthetic sulfur bacteria in waste stabilization ponds was conducted by Green in 1966 (18). Apparently the brown color imparted sometimes to the pond occurs when the concentration of sulfide in the pond is high and the photosynthetic bacteria store the sulfur as sulfur granules in the cell; when the sulfide concentration decreases and the sulfur granules are oxidized by the cell, the color imparted by photosynthetic sulfur bacteria is a vivid red. Due to their photosynthetic activity, this group of bacteria does not help to reduce the BOD of the wastes treated and may even tend to increase it (18). It should be remembered that this photosynthetic activity does not produce any molecular oxygen. When photosynthetic sulfur bacteria appear in a pond, they are initially found in the middle zone (zone 2, Fig. 2.2). In this zone anaerobic conditions exist and both light and hydrogen sulfide are available. Thus, the cell concentration tends to increase and, if the environmental conditions are favorable, the cells will rise to the top layer of the pond where better illumination is found.

The presence of photosynthetic sulfur bacteria has also been reported in several lakes with similar effects. Detailed studies have

been made on Lake Mendota (58).

## 2.3 - Theory of Hydrogen Sulfide Transfer

The largest part of this investigation deals with the study of sulfide concentration in waste stabilization ponds; however, environmental problems occur when hydrogen sulfide is released into the atmosphere. Therefore, a brief discussion is provided on the mechanism of transfer of hydrogen sulfide from ponds to the atmosphere.

A review is given of the general concepts of physical-chemical equilibrium of gases and their transfer from liquid to gaseous systems. This background is applied to the particular case of hydrogen sulfide.

According to Henry's law the equilibrium concentration of dissolved gas in a liquid is proportional to the partial pressure of that gas:

$$p = H\,x \qquad (2.9)$$

where:

- $p$ = partial pressure of the solute in the gas phase
- $x$ = mole fraction of the solute in the liquid phase
- $H$ = proportionality constant (temperature dependent)

In Table 2.1 are presented the values of H (proportionality constant) for different temperatures for a hydrogen sulfide-water system (54, p 667). In this same table may be found the hydrogen sulfide concentrations in air

TABLE 2.1

Equilibrium Characteristics of $H_2S$ in Water

| Temperature ($^{o}C$) | Henry's Constant H ($\frac{\text{atmospheres}}{\text{mole fraction}}$) | $H_2S$ Concentration in Air Necessary to Maintain Equilibrium with an $H_2S$ Concentration in Water of 2 mg/l ($mg/m^3$) | $H_2S$ Concentration in Air Necessary to Maintain Equilibrium with an $H_2S$ Concentration in Water of 0.1 mg/l ($mg/m^3$) |
|---|---|---|---|
| 0 | 268 | 217 | 10.85 |
| 5 | 315 | 255 | 12.75 |
| 10 | 367 | 297 | 14.85 |
| 15 | 423 | 342 | 17.10 |
| 20 | 483 | 390 | 19.50 |
| 25 | 545 | 441 | 22.05 |
| 30 | 609 | 492 | 24.60 |
| 35 | 676 | 547 | 27.35 |
| 40 | 745 | 604 | 30.20 |
| 45 | 814 | 658 | 32.90 |

necessary to maintain equilibrium with hydrogen sulfide concentration in water of 2 and 0.1 mg/l. It may be noted that the American Conference of Governmental Industrial Hygienists has set a threshold limit value for hydrogen sulfide concentration in air of 15 $mg/m^3$ (70). When the hydrogen sulfide concentration in air is 15 $mg/m^3$ the equilibrium hydrogen sulfide concentration in water at 20°C is less than 0.1 mg/l.

When equilibrium conditions do not exist the rate of exchange can be expressed with a simplified form of Fick's diffusion equation (4, p 444):

$$q = k (C - Ceq) \qquad (2.10)$$

where:

- q = flux of gas from liquid to atmosphere per unit area, per unit time
- C = gas concentration in liquid phase
- Ceq = equilibrium gas concentration in liquid phase
- k = proportionality constant

For hydrogen sulfide the problem is a little more complicated due to the double ionization of the hydrogen sulfide molecule (21, p 63):

$$H_2S \rightleftharpoons HS^- + H^+ \qquad (2.11)$$

the equilibrium relation being:

$$\frac{f[H^+] \cdot f[HS^-]}{f[H_2S]} = 1.1 \times 10^{-7} \quad \text{at } 25^\circ C \qquad (2.12)$$

and:

$$HS^- \rightleftharpoons S^= + H^+ \qquad (2.13)$$

the equilibrium relation being:

$$\frac{f[H^+] \cdot f[S^=]}{f[HS^-]} = 1 \times 10^{-14} \quad \text{at } 25^\circ C \qquad (2.14)$$

At pH 7.0 about 50% of the sulfide exists as $H_2S$, about 50% appears as $HS^-$, and a negligible amount occurs as $S^=$. At pH 8.0 about 8% of the sulfide exists as $H_2S$, 92% as $HS^-$ and a negligible amount as $S^=$.

The sulfide present in solution may be chemically oxidized by either dissolved oxygen or by some other oxidizing agent. For molecular oxygen the oxidation proceeds in a step-wise fashion as follows (7, p 40):

$$H_2S + \frac{1}{2} O_2 \longrightarrow S + H_2O \qquad (2.15)$$

$$S + O_2 \longrightarrow SO_2 \qquad (2.16)$$

the summary of these reactions being:

$$H_2S + 1.5\ O_2 \longrightarrow SO_2 + H_2O \qquad (2.17)$$

When the oxidation reaction is complete, 1.5 parts of oxygen are required to oxidize 1 part of sulfide. Dissolved iron is a catalyst for the oxidation reaction of sulfide by molecular oxygen.

The procedure used in this investigation to study the rate of transfer of hydrogen sulfide consisted in the determination of the rate of

disappearance of sulfide in water samples that were in contact with air or carbon dioxide.

The following observations are of significance:

1. At constant pH the relation between hydrogen sulfide concentration and total sulfide concentration is a constant.
2. The rate of sulfide disappearance from the water is affected by the chemical oxidation of sulfide. The chemical oxidation can be due to: (a) the dissolved oxygen already present in the water at the start of the experiment, and (b) to that oxygen that might enter the water during the experiment.
3. For a hydrogen sulfide-free atmosphere and a pH in the water of less than 5.0, the rate of sulfide disappearance due to $H_2S$ escape can be expressed as a function of Fick's diffusion constant as follows:

$$q = k \cdot c \tag{2.18}$$

$$Q = A \cdot q = A \cdot k \cdot c \tag{2.19}$$

$$Q = V\frac{dc}{dt} \tag{2.20}$$

$$V\frac{dc}{dt} = A \cdot k \cdot c \tag{2.21}$$

$$\ln c = \ln c_o - k \cdot \frac{A}{V} \cdot t \tag{2.22}$$

where:

V = volume of water sample

$A$ = area in contact with the atmosphere

$q$ = flux of gas per unit area, per unit time

$Q$ = flux of gas per unit time

$c_o$ = sulfide concentration at time zero

$c$ = sulfide concentration at time t

In a plot of ln c versus $t \cdot \frac{A}{V}$ the rate of disappearance appears as a straight line; the slope of this line represents the rate of transfer "k". When the pH in the water sample is above 5.0, the slope of the line represents the rate of transfer "k" divided by the relation (hydrogen sulfide concentration)/(total sulfide concentration).

When sulfide is added to the water it will reduce the dissolved oxygen present in the water, and as a consequence an imbalance will appear between the concentration of dissolved oxygen in the water and the partial pressure of oxygen in the air. Thus, more oxygen will enter into the water and more sulfide will be oxidized. Therefore, the rate of supply of oxygen to the solution will define the rate of sulfide disappearance in the sollution, due to oxidation.

The rate of oxygen diffusion into the water has been the object of extensive studies. In sanitary engineering the coefficient of oxygen diffusion has been studied in reference to stream sanitation and oxygenation of wastes. The diffusion constant has been found to vary widely with the particular physical conditions. Ippen et al (28, 29)

reported $k_w$ values ranging from 0.07 to 2.95 m/hr when air bubbles rise through water. In so e stream reaeration, O'Connor et al (46) report a $k_w$ value of 0.077 m/hr. Wheatland (73) reports a $k_w$ value of 0.107 m/hr $\left(0.244 \text{ (gms)}/(\text{ft}^2 \cdot \text{day} \cdot \text{mg/l})\right)$ for a laboratory system using a beaker and stirrer, and while limiting turbulence to a condition which preceeds vortex formation. The values of $k_w$ are highly dependent on the rate of renewal of the interphase film. Under quiescent conditions both the renewal rate and the oxygen diffusion rate are smaller.

The rate of sulfide disappearance due to oxidation by diffused atmospheric oxygen can be expressed as a function of $k_w$ as follows:

$$V \frac{dc}{dt} = k_w \cdot c_s \cdot A \cdot 1.5 \qquad (2.23)$$

$$c = c_o - 1.5 \cdot k_w \cdot c_s \cdot \frac{A}{V} \cdot t \qquad (2.24)$$

where:

$k_w$ = rate of oxygen diffusion into the water

$c_s$ = saturation concentration of dissolved oxygen

c, $c_o$, t, A, and V as defined before

The 1.5 factor in Eqs. 2.23 and 2.24 accounts for the stoichiometric relation in the oxidation reaction. Equations 2.23 and 2.24 were derived assuming an instantaneous oxidation reaction.

In a plot of logarithm of sulfide concentration at time, t, versus $t \cdot \frac{A}{V}$, Eq. 2.24 will not plot a straight line but will be concave downwards:

$$\ln c = \ln \left(c_o - 1.5 \cdot k_w \cdot c_s \cdot t \cdot \frac{A}{V}\right) \qquad (2.25)$$

$$\frac{d(\ln c)}{d(\frac{A}{V} \cdot t)} = -\frac{1.5 \cdot k_w \cdot c_s}{c} \qquad (2.26)$$

$$\frac{d^2(\ln c)}{d(\frac{A}{V} \cdot t)^2} = -\left(\frac{1.5\, k_w \cdot c_s}{c}\right)^2 \qquad (2.27)$$

Accepting what has been said so far, the following points should describe the experiment:

1. If at the beginning of the experiment the water sample contains oxygen, there will be a faster decrease in sulfide concentration initially, as compared to the later stages of the test.

2. Discounting the initial faster rate described under (1) above, the rate of disappearance should appear as a continuous function corresponding to the combined effects of two factors, namely (a) rate of oxygen diffusion into the water, Eqs. 2.23 through 2.27, and (b) rate of hydrogen sulfide gas escape, Eqs. 2.18 through 2.22.

Chapter 3

# DESCRIPTION OF THE EXPERIMENTS

In this chapter are described the physical model and the experimental procedures used in the different tests. The chapter is divided into four sections.

Section one describes the waste stabilization ponds and the procedure followed in the operation of the model. This section also includes a discussion of the factorial design of the tests made in this model. In section two are described the procedures followed in the quantitative determinations of the gaseous release of hydrogen sulfide. Section three deals with the qualitative analysis of the gases exchanged between the model and an enclosed air volume in contact with the pond surface. In section four are discussed the physical models and experimental procedures used in the study of the transfer of hydrogen sulfide from water to the atmosphere.

## 3.1 - Pond Experiments

The description of the experiments in the model pond will be presented in three parts, namely: (a) description of the physical model, (b) operating procedures, and (c) factorial design of the experiments.

Model Pond: The test apparatus consists of two metal drums welded together forming a cylinder with an inside diameter of 58.5

cm and total inside depth of 175 cm. Allowing 10 cm for free board and 5 cm. for sediments, the effective volume of the model is 430 liters. The surface area is 0.27 $m^2$ ($6.69 \times 10^{-5}$ acres). A cross-section of the model is presented in Fig. 3.1. Two of these units were used during these experiments. The interior walls of the iron drums were cleaned and painted with resin paint to inhibit corrosion. Surface illumination was provided on a twelve-hour on and off basis. The light assembly consisted of a 60-watt incandescent bulb and a 94-watt fluorescent tube. This light assembly was located 30 cm above the water surface, and it provided a light intensity of about 600 to 800 ft-candles near the water surface. The lighting system was enclosed in a hood which overlapped with the top of the pond unit (Fig. 3.1). The air enclosed by the hood could be sealed with aluminium foil fixed with masking tape. To simulate wind effects two systems were tried; one consisted of releasing pressurized air against the water surface. The second system consisted of a rod attached to a motor. The rod was submerged about 0.5 of an inch and it was slowly rotated (2 rpm), providing a gentle surface mixing. When the second system was used the temperature inside the hood and near the surface of the water increased during light periods to 35°C (95°F). When the first system was used the continuous renovation of the air inside the hood prevented this rise in temperature. For this reason the surface mixing with air jets was finally adopted for most of the tests.

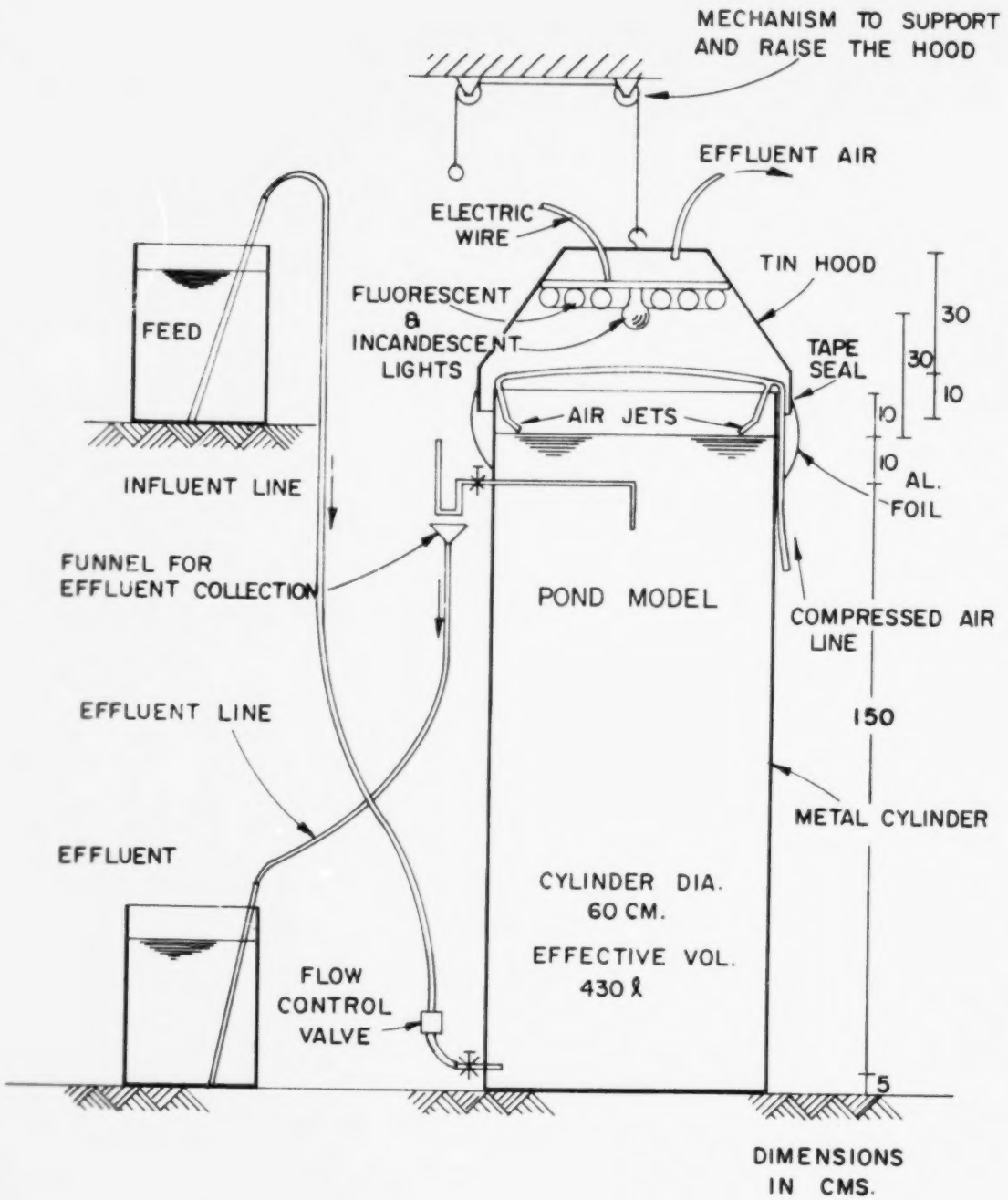



FIG. 3.1.—CROSS SECTION OF MODEL WASTE STABILIZATION POND

Operating Procedure: The unit was fed on a continuous basis with a synthetic waste. Fresh feed was prepared every twenty-four hours. The unit was fed by gravity through the bottom of the pond and the rate of flow was controlled with a valve in the feed line. The effluent was taken from the center of the pond at a depth of 20 cm.

The synthetic substrate was prepared with tap water and powdered milk. Potassium phosphate ($K_2HPO_4$) was added as a buffer and as an additional source of phosphorus. This type of synthetic substrate has been successfully used several times in stabilization pond studies (1, 21).

The powdered milk, "Starlac", is a product of "The Borden Company". The carbonaceous and nitrogenous oxygen demand of this substrate are shown in a long-term oxygen demand plot shown in Fig. 1 and Table 1 of the Appendix. The observed BOD/(Starlac concentration) is 0.66 with a reaction rate (k) equal to 0.75 days$^{-1}$. The nitrogenous oxygen demand is about 40% of the carbonaceous oxygen demand. The approximate chemical composition of "Starlac", Table 3.1, was provided by the manufacturer (Borden Fact Sheet FC/IS/46d64/RLR, The Borden Company, New York 17, New York). Chemical determinations of total N in the substrate yielded a value of 5.4 gm of nitrogen per 100 gm of Starlac. This yield represents about 14% of the protein content given by the manufacturer (Table 3.1, 36 gm of protein per 100 gm of Starlac), and about 8% of the substrate BOD (at 5 days

TABLE 3.1

Chemical Composition of Starlac

| Material | Concentration (gm/100 gm) |
|---|---|
| Protein | 36.0 |
| Lactose | 51.0 |
| Milk fat | 0.8 |
| Minerals | 8.2 |
| Calcium | 1.3 |
| Phosphorus | 1.0 |
| Iron | 0.0006 |
| Sodium | 0.525 |
| Potassium | 1.725 |
| Thiamine | 0.00034 |
| Riboflavin | 0.00193 |
| Niacin | 0.00106 |
| Cobalamin | 0.0000055 |
| Folic Acid group | 0.0000033 |
| Pantothemic Acid | 0.0035 |
| Pyridoxine | 0.0007 |
| Ascorbic Acid | 0.007 |
| Essential Amino Acids | |
| Arginine | 0.362 |
| Histidine | 0.271 |
| Isoleucine | 0.635 |
| Leucine | 0.965 |
| Lysine | 0.784 |
| Methionine + Cystine | 0.362 |
| Phenyl alanine + Tyrosine | 1.0 |
| Threonine | 0.452 |
| Tryptophan | 0.151 |
| Valine | 0.694 |

and 20° C). Chemical oxygen demand analysis of the substrate gave a COD/(Starlac concentration) relationship of 1.0.

$K_2HPO_4$ was added at a rate of 7.5 gm per 100 gm of Starlac. This gives a (phosphorus concentration)/(BOD - 5 days) relationship of about 2.5%.

The sulfate concentration in the tap water used to prepare the substrate averaged 23 mg/l (as $SO_4$). When required the sulfate concentration was adjusted by addition of ammonium sulfate $[(NH_4)_2SO_4]$.

With the procedures just described, the hydraulic load to the pond, the influent BOD, and the concentration of sulfate in the influent could be controlled. These parameters, of course, define the detention time, organic surface load (lbs BOD/acre/day) and sulfate surface load (lbs $SO_4$/acre/day).

The desired operating characteristics were adjusted for each of the experiments undertaken in these models and the pond operated for at least one detention time before the starting of a sampling and analysis program. The stability conditions of the pond were checked by determining the COD of the effluent over several consecutive days.

Once stability was reached, sampling and analysis were started. The procedures for the testing program were as follows:

a. Dissolved oxygen was measured with a galvanic cell oxygen analyzer. The probe containing the electrodes could be submerged to the bottom of the pond. The relation between readings in the

galvanometer and dissolved oxygen concentrations was previously determined using the Winkler method for dissolved oxygen determinations (64). The sensitivity of this probe is highly dependent on the water temperature. A comprehensive discussion of the relation between sensitivity and temperature is given by Mancy and Westgarth (37):

$$\frac{d\phi}{dT} = m\frac{\phi}{T} \tag{3.1}$$

$$\ln \phi = -\frac{m}{T} + b \tag{3.2}$$

where:

$\phi$ = instrument sensitivity = (reading in the galvanometer)/(dissolved oxygen concentration)

T = absolute water temperature

m = proportionality constant

b = integration constant

The sensitivity is also dependent on the conditions of the membrane. The characteristics of these membranes can change with time, so new calibrations had to be made at frequent intervals. One of these calibration curves is shown in the Appendix (Table 2, Figure 2).

This method of dissolved oxygen determination has been used in actual ponds with good results by Marais and Beer (39).

b. A calomel electrode, glass electrode system was used to measure pH. A long, narrow glass tube was hermetically connected to the KCl chamber of a calomel electrode, and this tube was filled with saturated-KCl solution. The length of the tube was greater than the depth of the pond. So, when submerged, the hydraulic pressure of the KCl solution in the electrode was large enough to keep the flow of the electrolyte from the electrode to the medium. This modified calomel electrode is described in more detail by Aguirre and Gloyna (1, p 24). The electrodes were connected to a model N Beckman potentiometer.

c. The same calomel electrode described above in (b) plus a platinum electrode were used to measure oxidation-reduction potentials. The calibration of the ORP electrodes was made with a quinone-hydroquinone solution at different pH values. At 20°C the standard potential of the (quinone-hydroquinone)-($H_2$ electrode) cell is as follows (24):

| | |
|---|---|
| pH = 0 | 704 mv |
| pH = 3.97 | 473 mv |
| pH = 4.6 | 437 mv |

and the changes in standard potential at pH = 0 with temperature are as follows (3):

| | |
|---|---|
| 0°C | 718 mv |
| 10°C | 711 mv |
| 20°C | 704 mv |
| 30°C | 696 mv |

At 20°C the potential of the (saturated-KCl calomel electrode)-($H_2$ electrode) cell is 250 mv. The electrodes used in these experiments were calibrated with quinone-hydroquinone at 20°C and pH of 3.97 and 4.6. The significance of the oxidation-reduction potentials in waste treatment systems was discussed by Drynan and Gloyna (16). For bacterial systems in general the observation made by Hewitt (24, p.103) seems to be important:

> "...the electrode potential indicate the state of the dynamic equilibrium of the culture, between the activity of the cellular enzymes and the constituents of the medium.....protecting the electrodes from contact with the bacteria made no great difference to the electrode potential. It is the effects produced by the bacteria and no contact with the cells themselves that affects the potential."

A Beckman model N potentiometer was connected to the electrodes. The relation between reading in the potentiometer and oxidation-reduction potential, as given by the manufacturer is:

$$ORP = 60\ (7 - R) \qquad (3.3)$$

where:

ORP = potential in millivolts

R = reading in pH scale of potentiometer

d. Determinations of sulfide concentrations were made with a modified form of the colorimetric method recommended in Standard Methods for Analysis of Water and Waste Water (64, p 429). The recommended method consists in the production of methylene blue in the sulfide-containing sample. Methylene blue is produced in the sample by addition of aliquots amounts of para-amino di-methyl aniline in acid solution, and ferric chloride. The treated sample is then compared with a second sample, treated with sulfuric acid and ferric chloride, to which methylene blue is added until the color of the first sample is matched. A previous calibration must be made, by a titrimetric method, of the relation between amounts of methylene blue used to match the color and sulfide concentration. The disadvantage of this method is that the amine solution has a strong brown color that makes it difficult to compare with the second sample that contains only methylene blue. The modification made, during these experiments, to the recommended method consisted of using a double-beam spectrophotometer. In order to avoid the interference of the brown color, a sample without sulfide and treated with the amine solution was placed in the reference beam. The maximum absorption of methylene blue occurs in the 670 - 680 mμ band. At this wave length a calibration was made between percent of light transmittance and concentration of sulfide in the sample. The advantages of the method are illustrated by the absorption spectras shown in Fig. 3 of the

Appendix, curve one corresponds to the absorption of a sample with zero sulfide concentration. All the absorption being due to the amine solution. Curve two shows the absorption of a sample containing 1.44 mg/l of sulfide. These two spectra were made with distilled water in the reference beam. Curve three shows the absorption of the sample with 1.44 mg/l of sulfide concentration, when a sample with amine solution is placed in the reference beam. The relation between sulfide concentration and transmittance is presented in the Appendix (Table 3, Fig. 4).

e. The rest of the analysis, including COD, BOD, solids, total-N, iron concentration, and sulfate concentration were made according to Standard Methods for Analysis of Water and Waste Water (64).

Factorial Design of the Experiment: The set of experiments made in the model pond were designed to study the production of hydrogen sulfide as a function of the operating characteristics of the pond.

The wide number of variables related to the production of sulfide in a pond can be discussed in two groups. The first group would include those variables that can be directly controlled by the designer of the pond, e.g., physical characteristics of the pond, detention time, organic surface load, etc. The second group of variables are such as depth of the aerobic layer in the pond, oxidation-reduction potentials, pH, etc.

With the results of the experiments described in this section, empirical relations were developed between the concentrations of

sulfide present in the model pond and some of the independent variables (i.e., variables of the first group). Records were kept during the different experiments of the observed values of the variables of the second group (i.e., the dependent variables).

For the development of the empirical relations mentioned above, six independent variables were considered:

1. organic surface load to the pond
   (lbs BOD/acre/day)
2. detention time (days)
3. surface loading of sulfate to the pond
   (lbs $SO_4^=$/acre/day)
4. sulfate concentration in the influent (mg/l)
5. sulfide surface load to the pond
   (lbs $S^=$/acre/day)
6. sulfide concentration in the influent (mg/l)

The number of variables to be considered in the design of the experiment was reduced to four. Variables (1) and (2), namely organic load to the pond and detention time, are two of the fundamental design parameters of a pond. They determine the rate of microbial activity in the pond, including the production of sulfide. For these reasons variables (1) and (2) were considered in the design of the experiment.

Of the four remaining variables the two dealing with sulfides, variables (5) and (6), were dropped. For some industrial wastes, the concentration of sulfides may reach values of 400 and 500 mg/l (44, p 299); however, for domestic wastes and for most industrial wastes, sulfide concentrations are much smaller. Sulfate concentration on the contrary can be found in higher concentrations. In domestic waste water this concentration depends on the sulfate concentration of the water supply. Many water supplies contain high concentrations of sulfates although the threshold limit for sulfate concentration in water supplies, as recommended by the Public Health Service, is 250 mg/l (15). For some industrial wastes, such as kraft-mill effluents, the sulfate concentration can exceed 400 mg/l (44, p 371). The importance of sulfate as a potential sulfide source, under anaerobic conditions, was indicated in Sections 2.1 and 2.2. After consideration of the facts just mentioned it was decided to keep variables (3) and (4), that deal with sulfates, and eliminate variables (5) and (6), that deal with sulfides.

A question might be raised regarding the independence of variables (3) and (4), dealing with sulfate concentration in the influent and sulfate surface load. That they are independent variables is clear when the following criteria of independence is considered: two variables are considered interdependent when a change in the value of either one of them implies a change in the value of the other. This

criteria does not make any reference to the values, or change of value of the other variables of the system.

In the model pond, the sulfate concentration in the influent and sulfate surface load might be considered independent, since changes in the value of either one of them can be made without changing the value of the other. This change in concentration was accomplished by appropriate changes in the hydraulic load (i.e., the detention time). However, the group formed by these three variables (detention time, sulfate influent concentration and sulfate surface load) is not a group of independent variables. The combination of these three variables was not used in the design of the experiment.

An experimental technique known as factorial design was used to decide on the characteristics of each test. Factorially designed experiments permit the development of empirical linear relations between the dependent function and the independent variables. The use of the factorial design technique in this investigation does not mean that the relation between sulfide production in a pond and the selected independent variables is believed to be a linear relation. But some sort of relation certainly exists and for a limited range of values of the independent variables, a linear approximation can be used. The goodness of the approximation can not be deduced from the results of the tests used to define the relation. In this

investigation the results of independent tests were used to check the accuracy of the empirical equations.

Three sets of tests were designed. Each set included a $2^3$ factorial experiment, i.e., each set was designed to permit an interplay of three variables with two possible values for each variable.

The combination of variables used in each set of tests were as follows:

1. BOD surface load (68 and 136 lbs BOD/acre/day)
   $SO_4$ influent concentration (23 and 200 mg/l)
   Detention time (15 and 30 days)
2. BOD surface load (68 and 136 lbs BOD/acre/day)
   $SO_4$ surface load (11 and 188 lbs $SO_4$/acre/day)
   Detention time (15 and 30 days)
3. BOD surface load (68 and 136 lbs BOD/acre/day)
   $SO_4$ influent concentration (200 and 400 mg/l)
   $SO_4$ surface load (94 and 188 lbs $SO_4$/acre/day)

The possible combinations of a system of three variables, with two levels for each variable, are graphically presented in Fig. 3.2. The number of possible combinations is $2^3$ (i.e., eight). Each corner of the cube shown in Fig. 3.2 represents one of these possible combinations.

The form of the empirical equations that can be developed with this method is as follows:

$$U = aX + bY + cZ + d \qquad (3.4)$$

where U is the dependent variable (sulfide concentration, in this case); X, Y, and Z are the three independent variables used in the set of experiments; and a, b, c, and d are the four coefficients to be computed from the results of the experiments. When the effects of the interaction of the three variables (i.e., the effects of XY, XZ, YZ, and XYZ) are desired, the number of coefficients to be computed is eight:

$$U = aX + bY + cZ + d + eXY + fXZ + gYZ + hXYZ \qquad (3.5)$$

In this investigation only the effects of the independent variables were studied; the effects of their interactions were not studied. In consequence only the four coefficients mentioned first (a, b, c, and d of Eq. 3.4) were computed. To determine these four coefficients, four simultaneous equations were used. The four simultaneous equations were formed with the results of sulfide concentration determinations obtained in four different experiments. Any four of the eight possible combinations of variables (Fig. 3.2) could be used; however, the factorial design technique permits a more rational selection of the combinations to be used. These combinations should represent points evenly distributed in the region of interest.

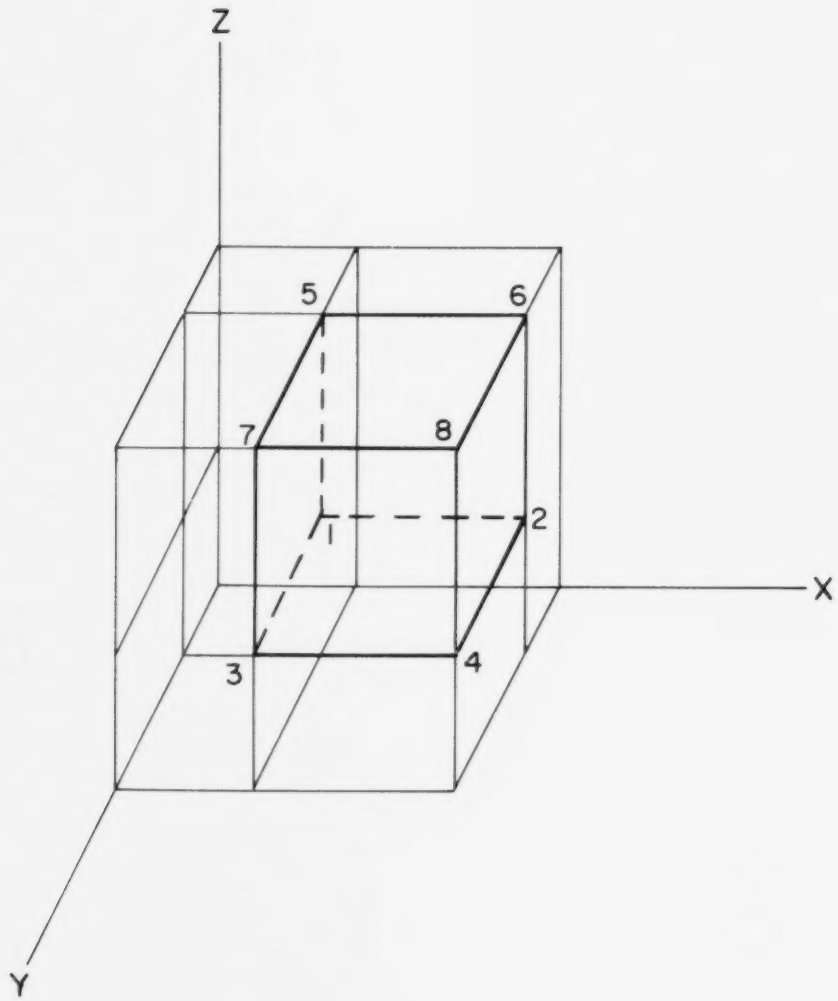



FIG. 3.2.—GRAPHIC REPRESENTATION OF THE POSSIBLE COMBINATIONS OF THREE VARIABLES WITH TWO LEVELS.

The selection of the four combinations of variables can be made as shown in Table 3.2. The two possible levels for each variable are indicated in Table 3.2 as high level (+) and low level (-). An extra column is presented with the arithmetic determination of the sign of the interaction of two of the independent variables. Variables X and Y are given in Table 3.2. In four of the eight cases the sign of the interaction XY is the same as the sign of the third variable (Z), namely: tests two, three, five, and eight. In the other four cases (tests one, four, six, and seven) the sign is different. Each one of these two sets of four tests corresponds to some combination of variables representing points evenly distributed in the zone of interest. The same result would have been obtained if variables X and Z or Y and Z had been used, instead of X and Y, to compute the sign of the extra column. In the design of the experiments undertaken in the model pond, the first group of tests (i.e., two, three, five and eight) were used. This technique for the design of experiments is explained in detail by Johnson and Leone (30).

The three sets of four experiments obtained in this manner with the three combinations and levels of independent variables are shown in Table 3.3. The letters and the signs in parentheses in Table 3.3 refer to the nomenclature used in Table 3.2. The fourth operating characteristic shown in Table 3.3 was computed with the following equation:

TABLE 3.2

Characteristics of the Eight Possible Combinations of Variables

| Test | Value of Independent Variables | | | Sign of Interaction XY |
|---|---|---|---|---|
| | X | Y | Z | |
| 1 | low (-) | low (-) | low (-) | (+) |
| 2 | high (+) | low (-) | low (-) | (-) |
| 3 | low (-) | high (+) | low (-) | (-) |
| 4 | high (+) | high (+) | low (-) | (+) |
| 5 | low (-) | low (-) | high (+) | (+) |
| 6 | high (+) | low (-) | high (+) | (-) |
| 7 | low (-) | high (+) | high (+) | (-) |
| 8 | high (+) | high (+) | high (+) | (+) |

TABLE 3.3

Characteristics of the Three Sets of Four Experiments

| Set | Test | Test Operating Characteristics | | | |
|---|---|---|---|---|---|
| | | BOD Surface Load (lb/acre/day) | $SO_4$ Influent Concentration (mg/l) | $SO_4$ Surface Load (lb/acre/day) | Detention Time (days) |
| (a) | 1 | (X) 136 (+) | (Y) 23 (-) | 23 | (Z) 15 (-) |
| | 2 | 68 (-) | 200 (+) | 188 | 15 (-) |
| | 3 | 68 (-) | 23 (-) | 11 | 30 (+) |
| | 4 | 136 (+) | 200 (+) | 94 | 30 (+) |
| (b) | 1 | (X) 136 (+) | 23 | (Y) 23*(-) | (Z) 15 (-) |
| | 2 | 68 (-) | 200 | 188 (+) | 15 (-) |
| | 3 | 68 (-) | 23 | 11 (-) | 30 (+) |
| | 4 | 136 (+) | 400 | 188 (+) | 30 (+) |
| (c) | 1 | (X) 136 (+) | (Y) 200 (-) | (Z) 94 (-) | 30 |
| | 2 | 68 (-) | 400 (+) | 94 (-) | 60 |
| | 3 | 68 (-) | 200 (-) | 188 (+) | 15 |
| | 4 | 136 (+) | 400 (+) | 188 (+) | 30 |

*This value should be 11, but due to the $SO_4$ concentration in tap water, it was not possible to lower it.

($SO_4$ surface load) · (detention time) = ($SO_4$ influent concentration) · (depth of the pond) (3.6)

Table 3.3 shows that many of the tests are common to either two or three of the sets. Actually the twelve tests shown in Table 3.3 involve only six different experiments. This reduction in the number of experiments required was made possible by the different levels of variables used in the different sets of experiments. With the arrangement just described three different empirical equations can be developed, and each equation can be checked for accuracy with the results of two independent experiments (the operating characteristics of the two independent experiments would not necessarily be in the range for which the equations were derived). A seventh test was undertaken in order to provide a third check of accuracy for each equation. The operating characteristics of the seven tests made (with the test identification that will be followed from now on) are shown in Table 3.4.

## 3.2 - Quantitative Determinations of Released Hydrogen Sulfide

Quantitative determinations were made of the hydrogen sulfide released by the pond unit. The determinations were made for periods of 12, 24 and 48 hours. The assembly used is shown in Fig. 3.3. The hood was sealed and the effluent air passed through a cadmium sulfate solution. The absorption mixture was prepared with 4.3 gm

TABLE 3.4

Test Identification and Characteristics

| Test Identification | Operating Characteristics | | | |
|---|---|---|---|---|
| | BOD Surface Load (lb/acre/day) | Sulfate Concentration (mg/l) | Sulfate Surface Load (lb/acre/day) | Detention Time (days) |
| 1 | 136 | 23 | 11 | 30 |
| 2 | 68 | 23 | 11 | 30 |
| 3 | 136 | 23 | 23 | 15 |
| 4 | 136 | 200 | 94 | 30 |
| 5 | 68 | 400 | 94 | 60 |
| 6 | 68 | 200 | 188 | 15 |
| 7 | 136 | 400 | 188 | 30 |

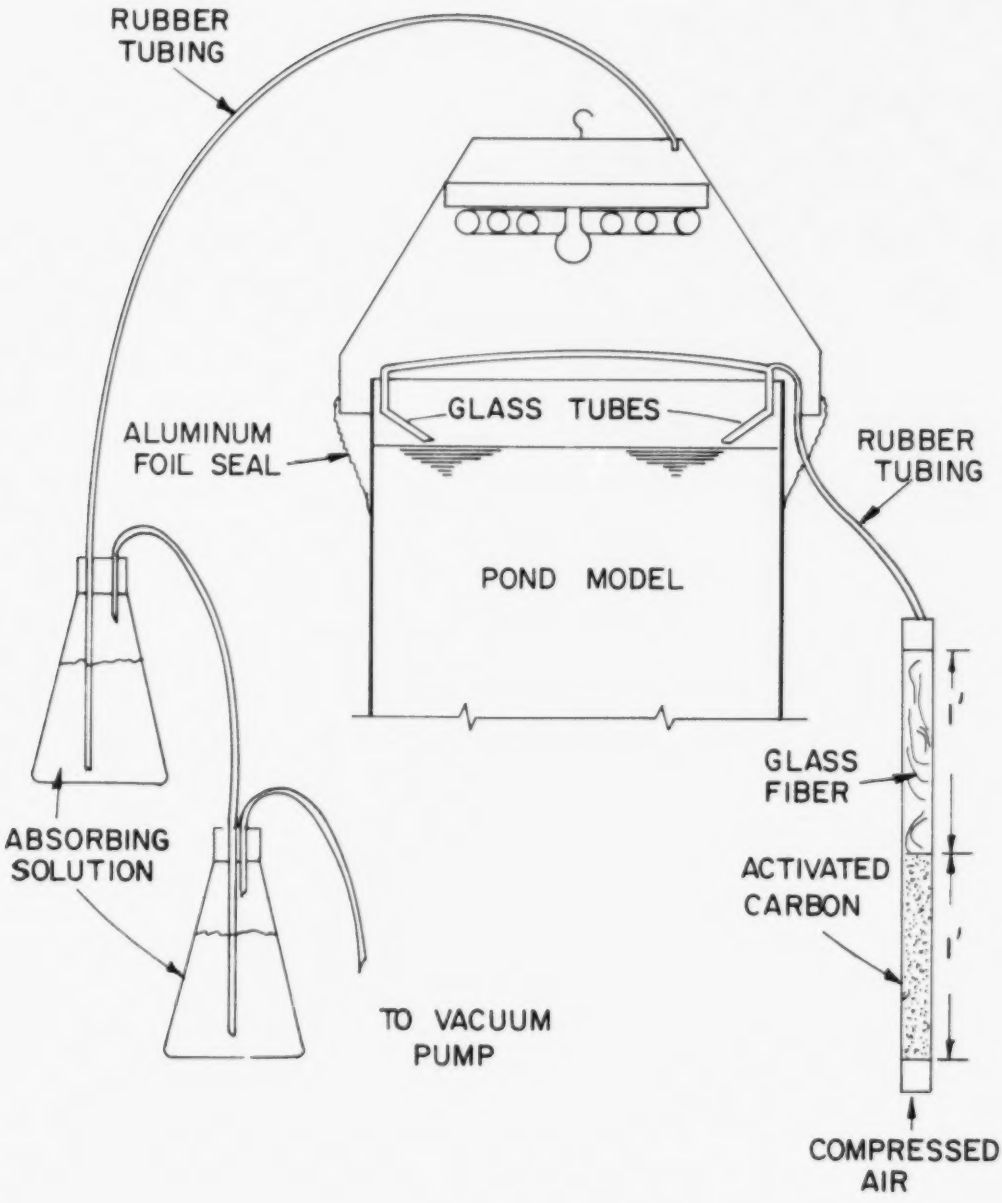



FIG. 3.3.—ASSEMBLY FOR QUANTITATIVE DETERMINATION OF HYDROGEN SULFIDE ESCAPED FROM POND

of 3 $CdSO_4 \cdot 8H_2O$ and 0.3 gm of NaOH dissolved in one liter of water (this formula was taken from a booklet of the Robert A. Taft Sanitary Engineering Center, Cincinnatti, Ohio, "Analysis of Atmospheric Inorganics", March 1964). When hydrogen sulfide is bubbled in the cadmium sulfate solution a precipitate of cadmium sulfide is formed, and this sulfide can then be determined chemically.

The assembly used to conduct the effluent gases to the absorbing solution had the disadvantage that hydrogen sulfide could be oxidized in the wet surface of the conducting lines, Fig. 3.3. The possible effects of this oxidation in the results obtained are discussed in the next chapter.

## 3.3 - Qualitative Analysis of Gases

An analysis was made of the changes in composition of an enclosed volume of air in contact with the surface of the pond. This analysis, conducted during Test 7, was made with infrared absorption spectroscopy. The gas collection assembly used is shown in Fig. 3.4. The analytical equipment included an infrared spectrophotometer by Beckman (IR 7) and a gas cell with a path length of 10 m.

The procedure followed in these tests is as follows:

1. Flush volume above pond for 2 to 3 hours with filtered air.
2. Take 6 liters of air sample, using the silica gel filter shown in Fig. 3.4, and obtain the infrared absorption spectrum "blank".

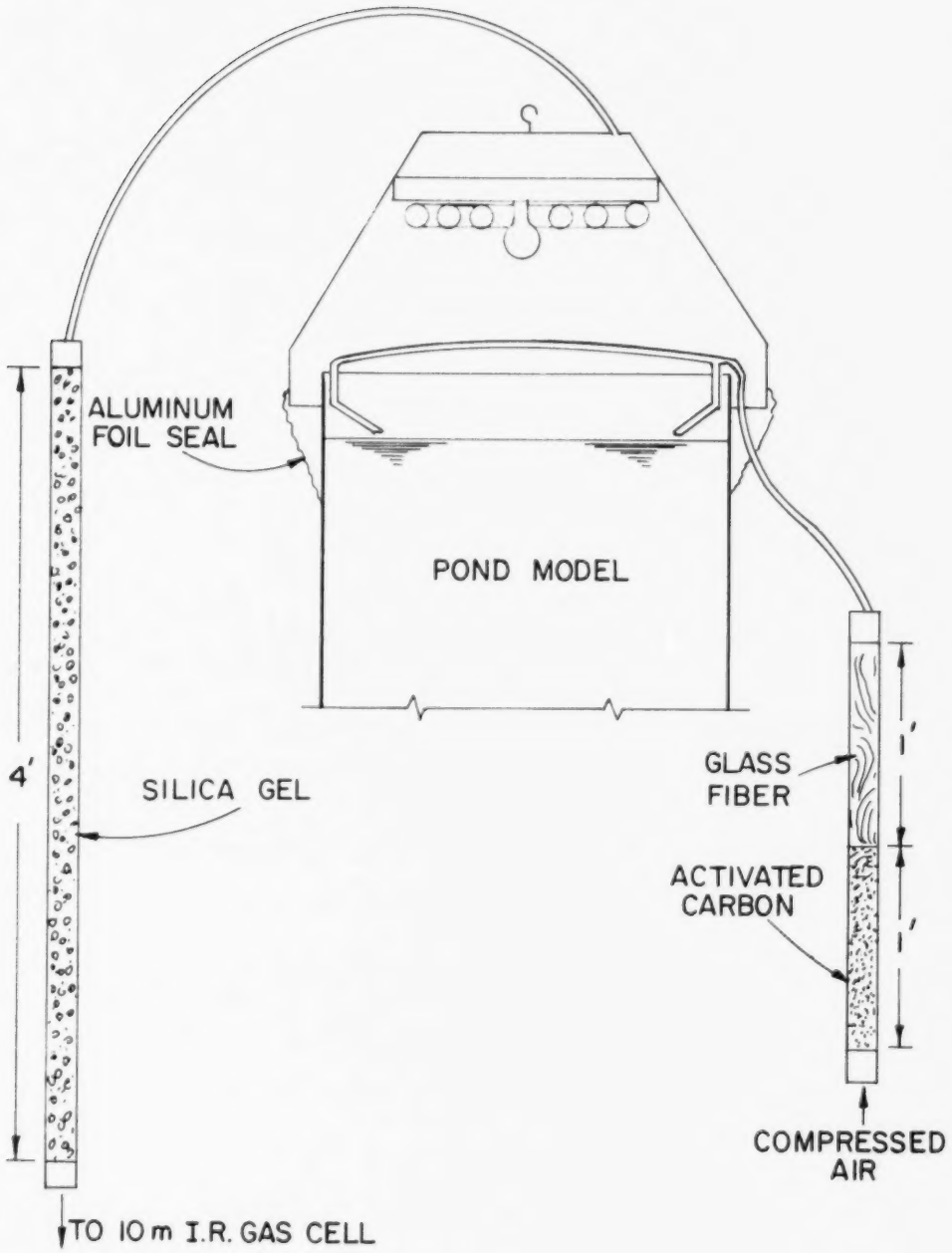



FIG. 3.4.—ASSEMBLY FOR GASES SAMPLING

3. Seal hood to pond unit and cut off the air flow.

4. Turn lights on; after 12 hours of illumination take a new air sample (6 L), following the same procedure used in (2) above, and obtain the infrared absorption spectrum. The spectrum so obtained was called the "8 PM Sample."

5. Repeat steps (1) through (4) above, but now with the lights off for a 12-hour period. The new spectrum was called the "8 AM Sample."

The volume enclosed by the hood was about 70 liters. Before taking the air sample, air trapped in the silica gel filter and in the lines was washed out. The reason for the silica gel filter was to remove as much moisture from the air as possible. The interference of water in the identification of other compounds with infrared analysis is discussed in the chapter of results. The biggest disadvantage of the silica gel filter is the possibility of other compounds being absorbed in this column during the sampling.

## 3.4 - Hydrogen Sulfide Transfer Rates

This section describes the experimental program and approaches used to determine the rate of hydrogen sulfide transfer from the water to the atmosphere. Three different types of experiments were undertaken.

Changes Due to Oxidation and Escape: A series of tests were made to determine the change in sulfide concentration in water samples open to the air. In these tests the changes in concentration were due to oxidation and escape of $H_2S$ to the atmosphere. The apparatus used for these determinations is shown in Fig. 3.5 (a). Both distilled and pond waters were used in volumes of one, two or three liters. At the start of the experiment the sulfide concentration was adjusted to about 20 mg/l. Sodium sulfide ($Na_2S \cdot 9H_2O$) was used to adjust the sulfide concentration. This compound is a strong basic salt and it caused the pH to rise above 9. Therefore, when desired the pH was reduced with dilute HCl. Also, the pH was buffered when the pH was in the 7 to 8 range. The buffer was prepared with citric acid and sodium phosphate ($NaHPO_4$) (20).

All solutions were gently mixed at the start of the experiment. This provided a uniform concentration. The samples were taken either from the center or from both the top and the bottom of the container. Sample volumes varied from 1 to 7.5 ml and no replacement of water was made to the original test container.

Oxygen Diffusion: The rate of oxygen diffusing from the air to the water was determined in these experiments for conditions similar to those described in the above paragraph. At the start of the experiment the water sample was purged of oxygen with nitrogen gas.

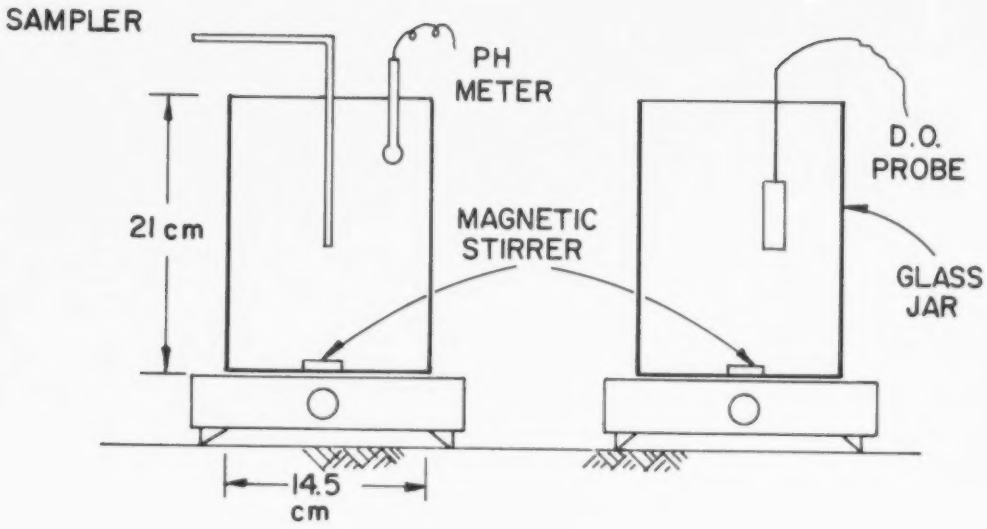



FIG. 3.5. – ASSEMBLY TO STUDY SULFIDE DISAPPEARANCE

Dissolved oxygen concentrations were read with a galvanic cell as shown in Fig. 3.5 (b).

Changes Due to Escape: In these experiments the rate of disappearance of hydrogen sulfide in the water was measured when no oxygen was present in the atmosphere in contact with the sample. The assembly used is shown in Fig. 3.6. A low flow of carbon dioxide was maintained at the surface in order to prevent air from entering the system.

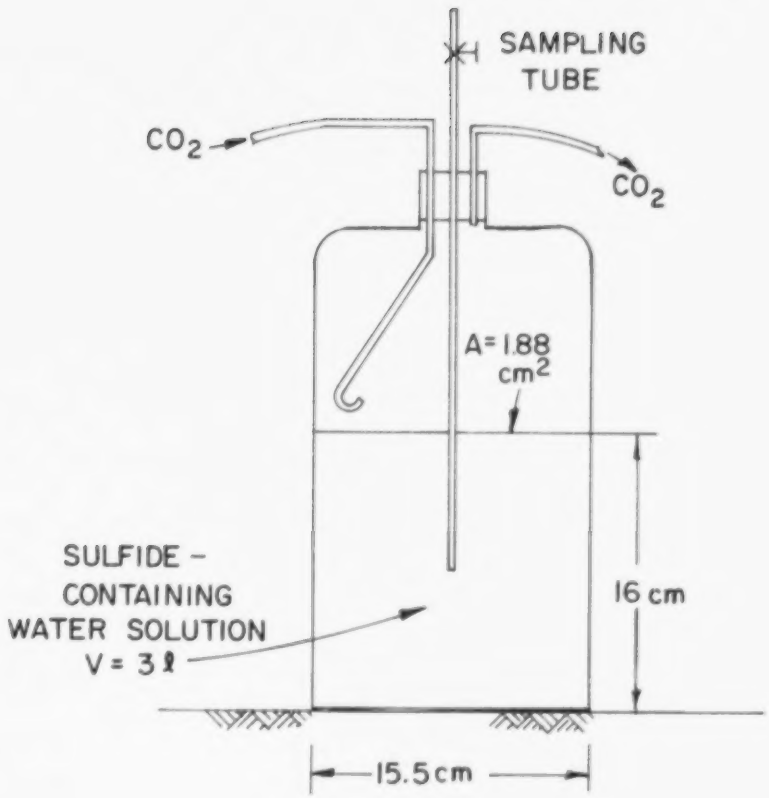



FIG. 3.6.–ASSEMBLY TO DETERMINE RATE OF ESCAPE OF HYDROGEN SULFIDE.

Chapter 4

# EXPERIMENTAL RESULTS, ANALYSIS AND INTERPRETATION

The presentation and analysis of results is divided into four sections: (a) results obtained in the operation of the model ponds and the development of empirical equations, (b) the measurement of escaped hydrogen sulfide, (c) infrared analysis of gases exchanged between the model pond and the atmosphere, and (d) discussion of hydrogen sulfide transfer rates.

## 4.1 - Model Pond Studies

The operation of the model pond and the empirical functions describing sulfide production are described.

Model Pond Results: In each of these experiments, Table 3.4, the model was operated until equilibrium was reached. Once stability was obtained, sulfide was measured, twice each day, along the depth of the pond. The measurements were made at 8 AM, when the lights were automatically switched on, and at 8 PM, when the lights were turned off. The two measurements were made to illustrate the effects of the algae and photosynthetic sulfur bacteria during light and dark periods. The tests included: sulfide, pH, ORP, COD, temperature, dissolved oxygen, light intensity, sulfate concentration, iron concentration and both fixed and suspended solids.

All the data collected in the seven experiments are presented in the Appendix (Tables 4 through 17). Figures 4.1 through 4.13

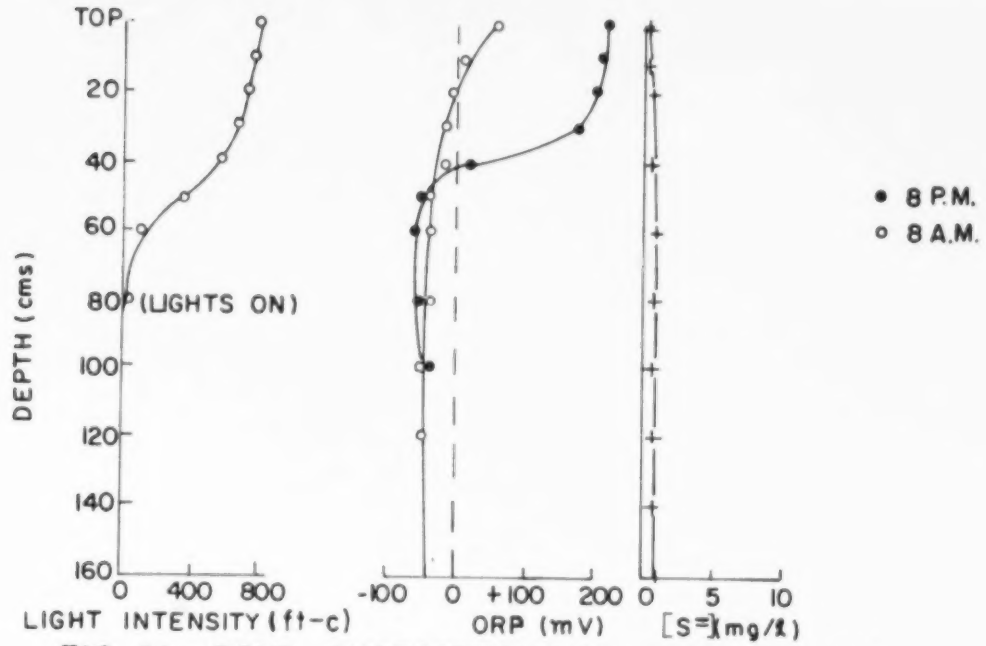



FIG. 4.1 — POND CHARACTERISTICS, TEST NO. 1 (a)

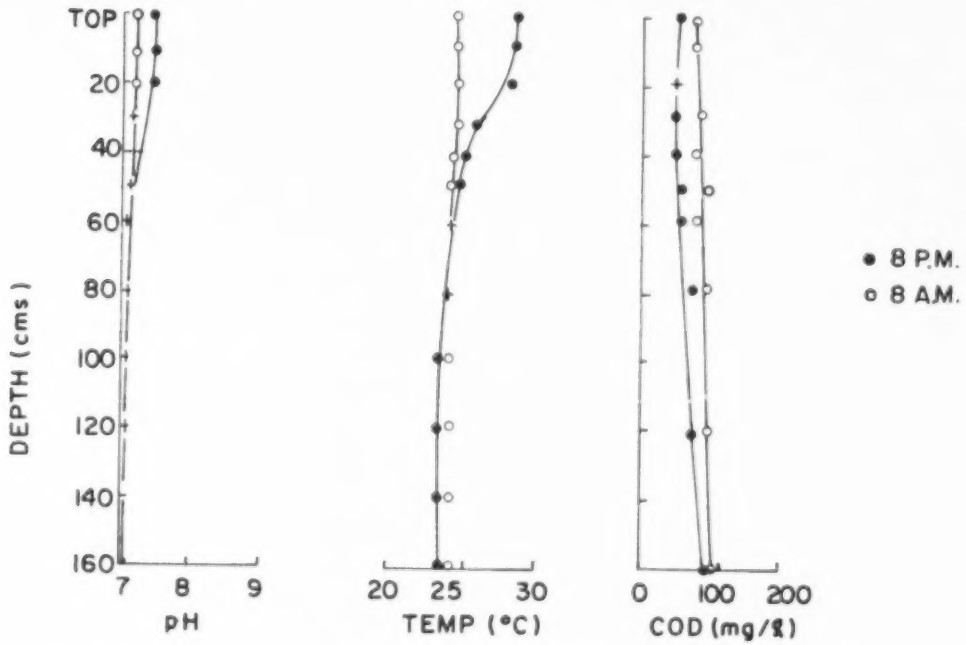



FIG. 4.2.-POND CHARACTERISTICS, TEST NO. 1 (b)

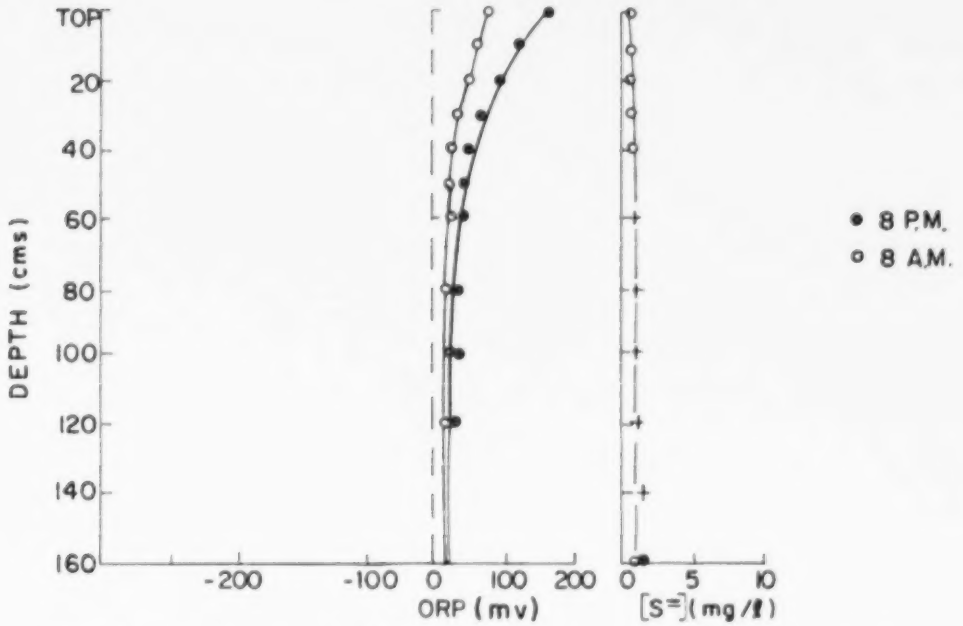



FIG. 4.3.-POND CHARACTERISTICS, TEST NO. 2 (a)

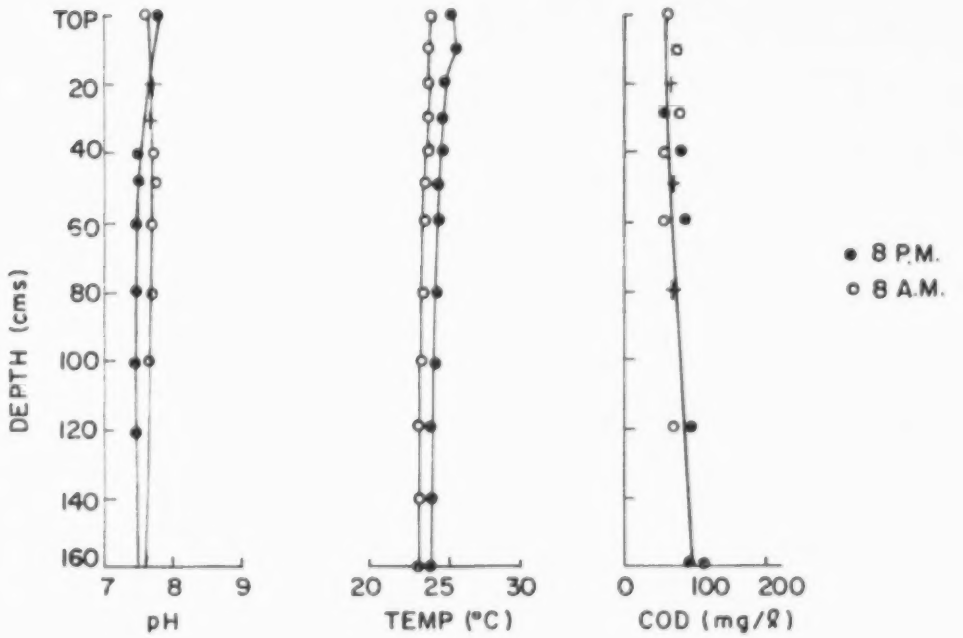



FIG. 4.4.-POND CHARACTERISTICS, TEST NO.2 (b)

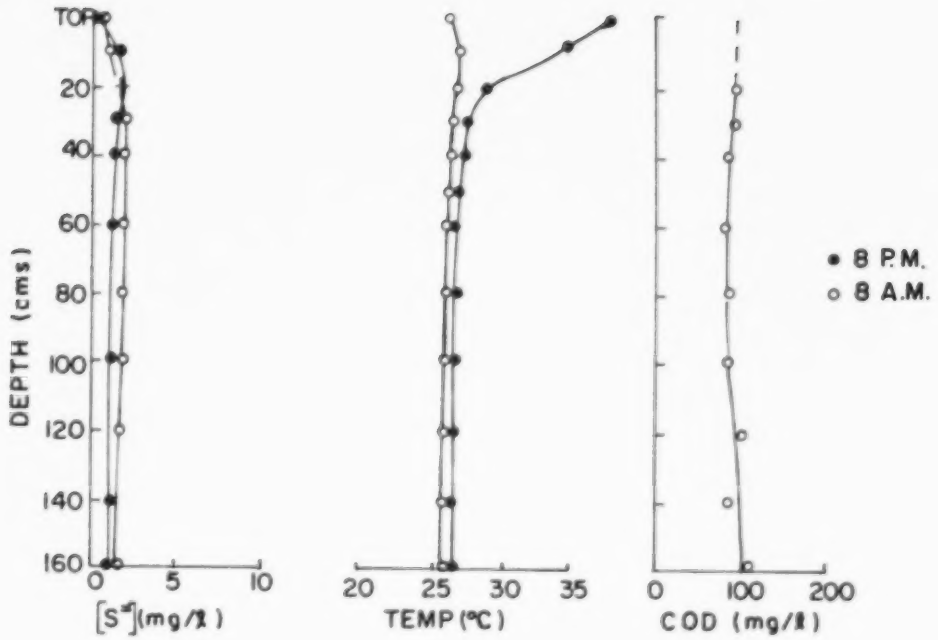



FIG. 4.5.-POND CHARACTERISTICS, TEST NO. 3

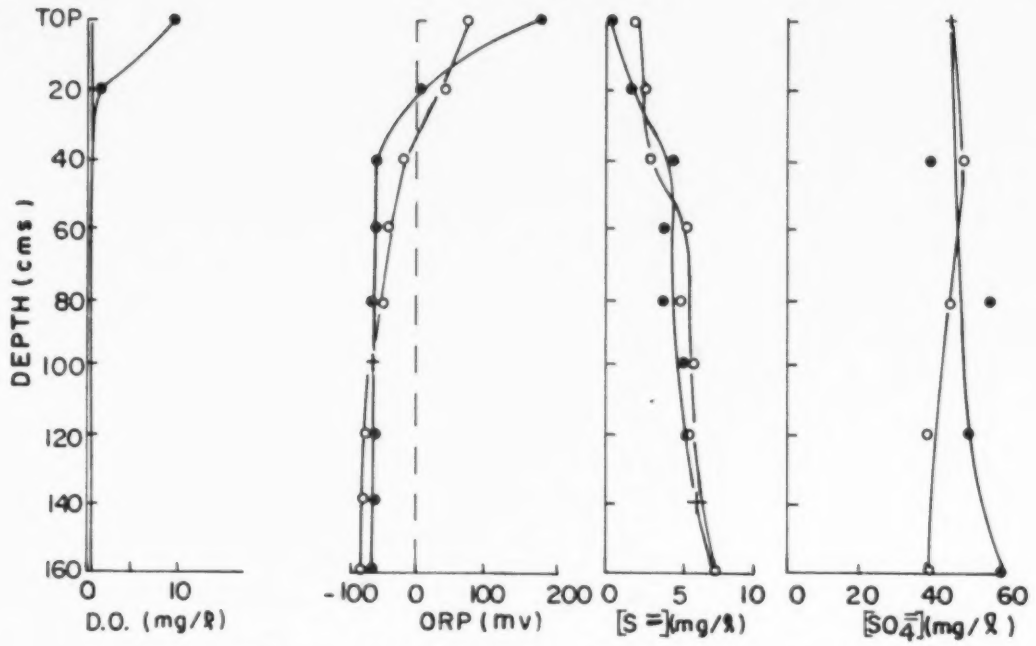



FIG. 4.6.- POND CHARACTERISTICS, TEST NO. 4 (a)

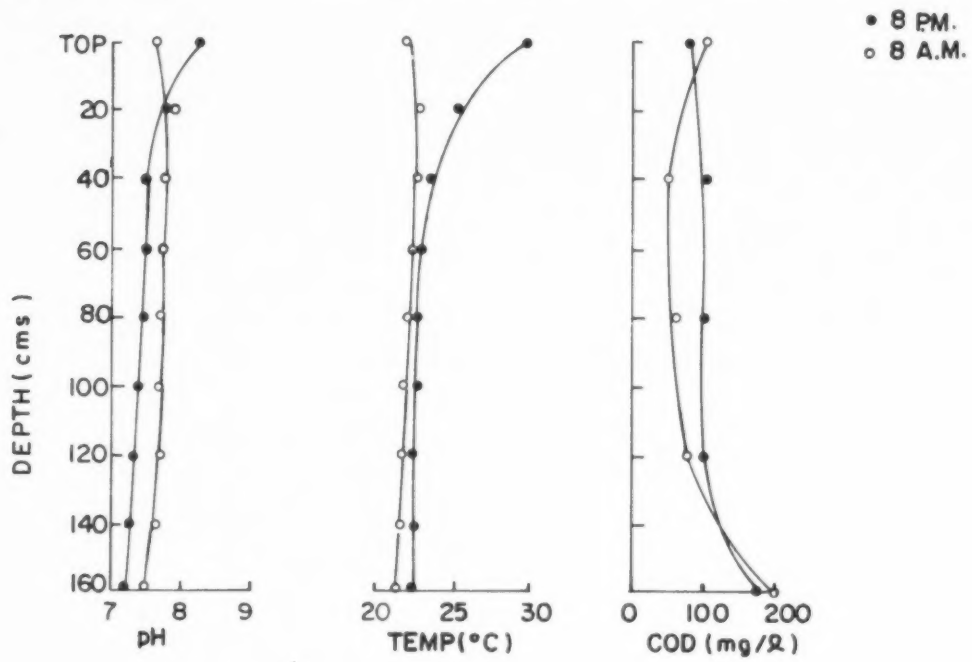



FIG. 4.7.- POND CHARACTERISTICS, TEST NO. 4(b)

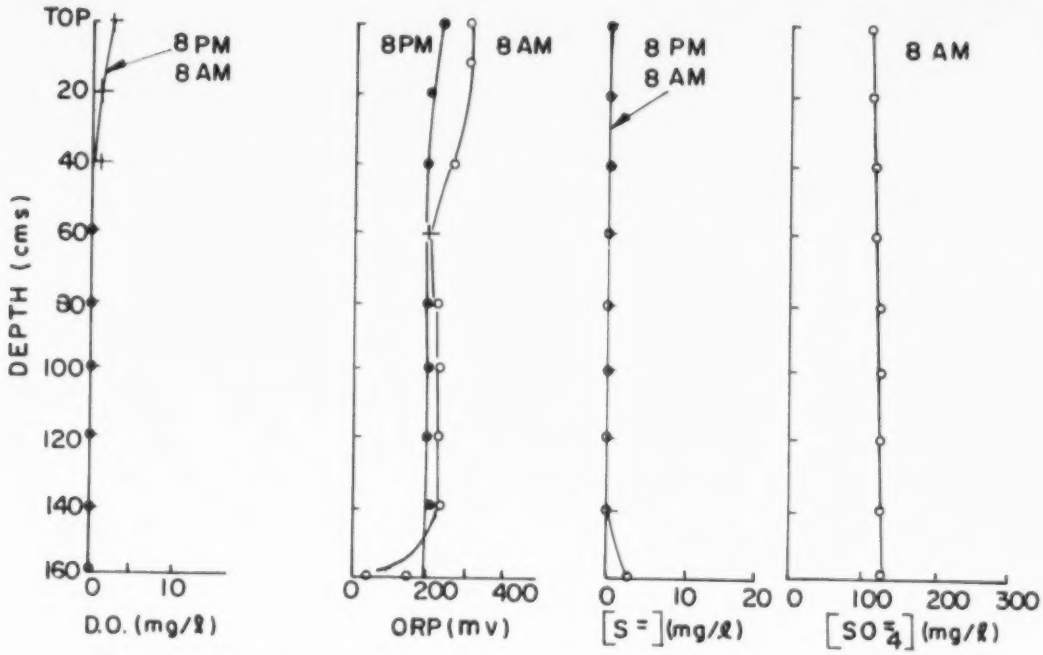



FIG. 4.8.-POND CHARACTERISTICS, TEST NO. 5 (a)

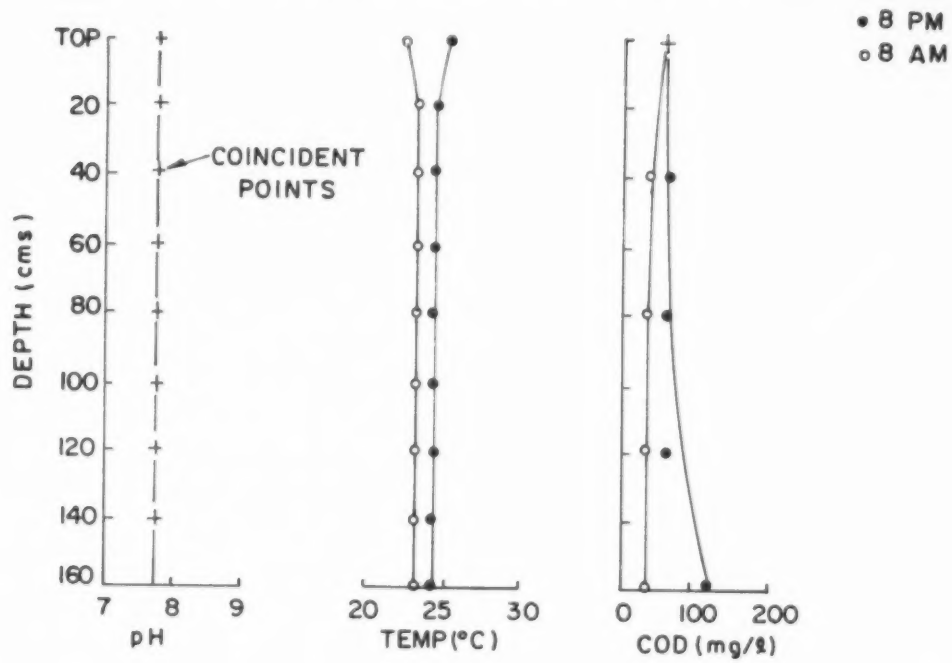



FIG. 4.9.-POND CHARACTERISTICS, TEST NO. 5 (b)

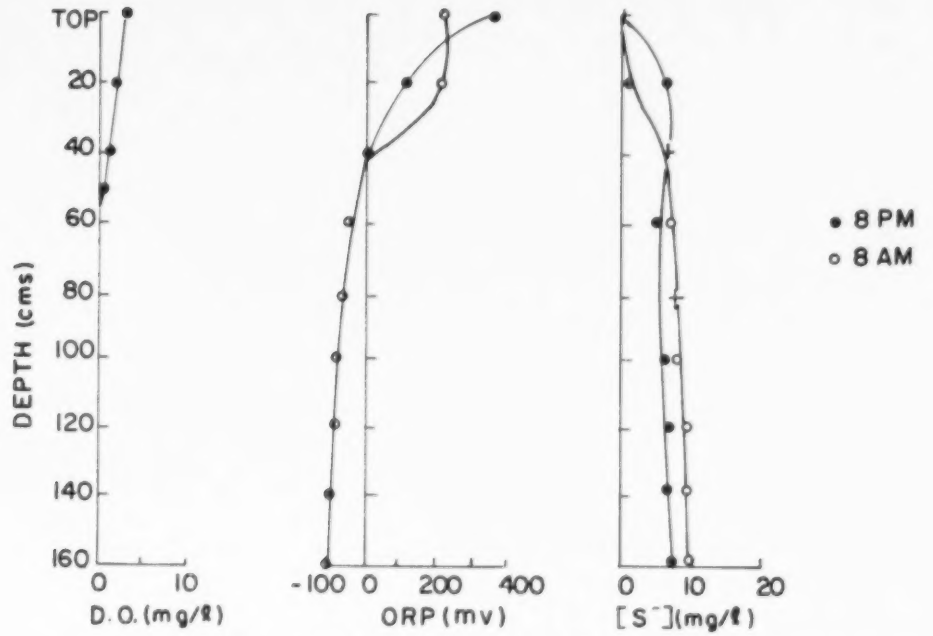



FIG. 4.10.- POND CHARACTERISTICS, TEST NO. 6 (a)

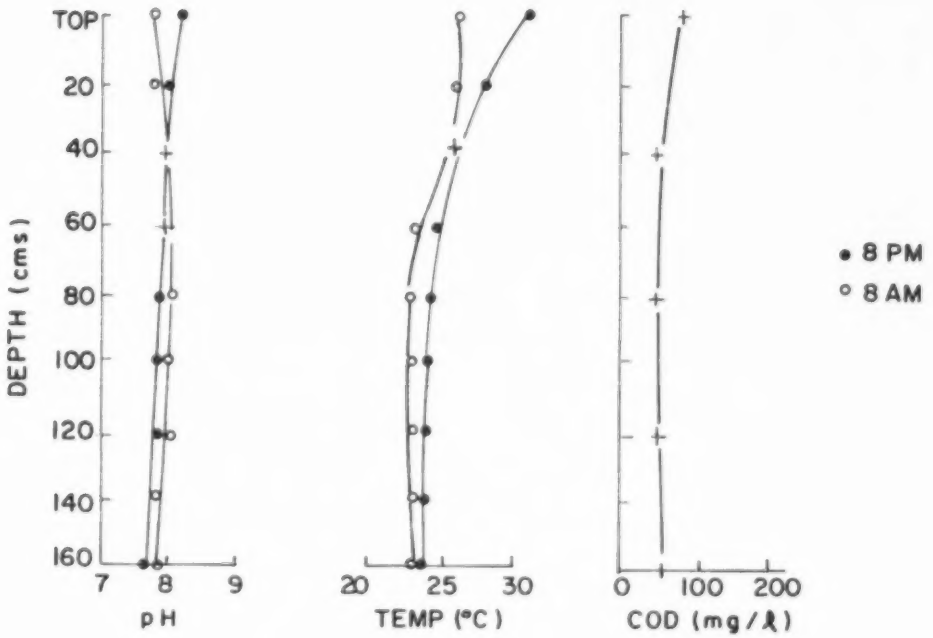



FIG. 4.11.- POND CHARACTERISTICS, TEST NO. 6 (b)

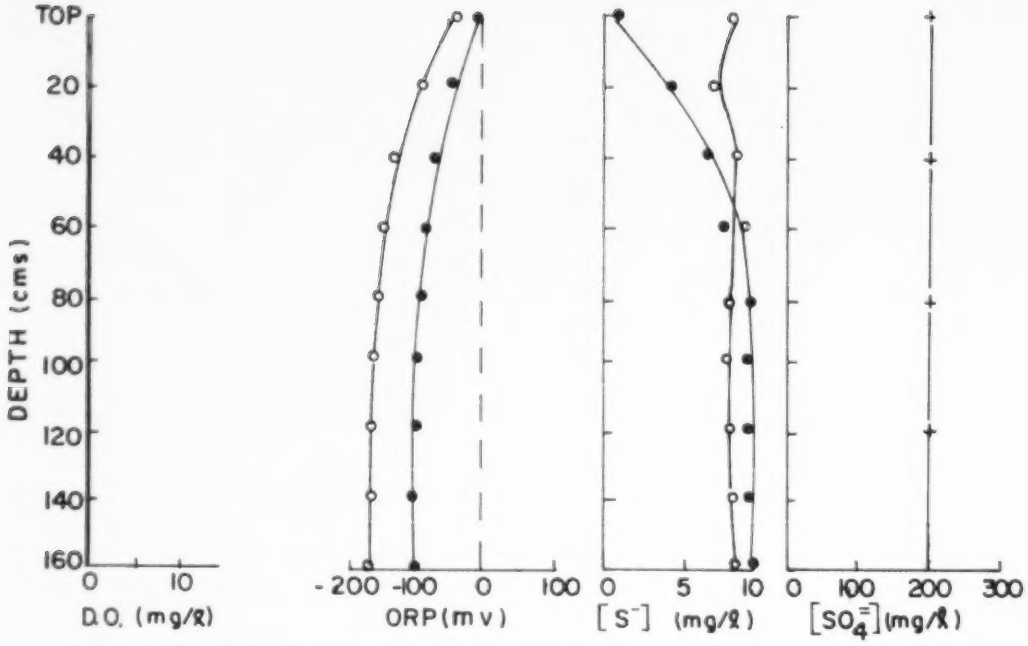



FIG. 4.12.-POND CHARACTERISTICS, TEST NO. 7(a)

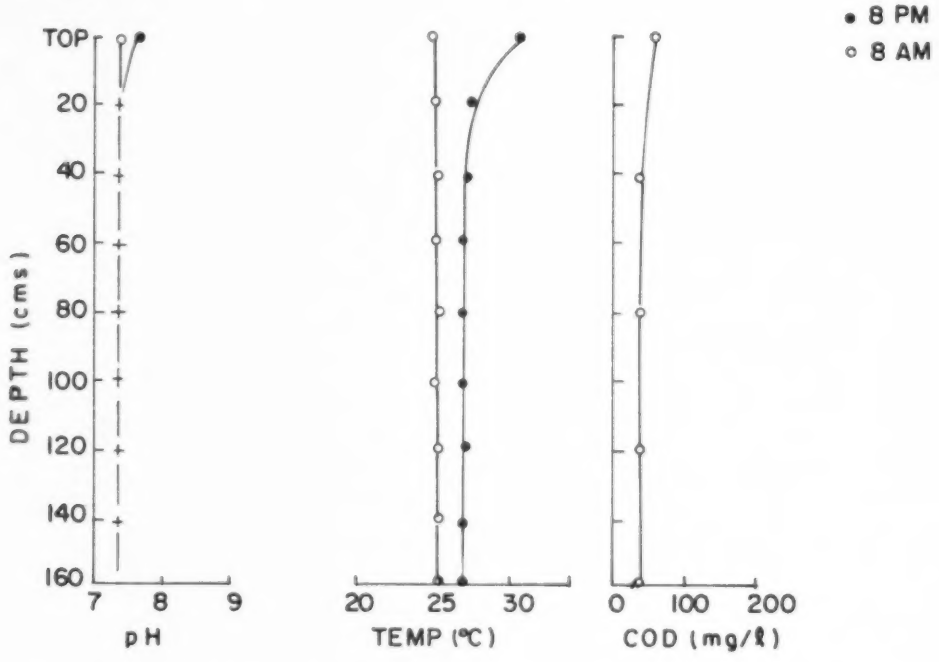



FIG. 4.13.-POND CHARACTERISTICS, TEST NO. 7(b)

illustrate various profiles along the depth of the pond. Some observations about the results follow:

1. Tests 3 and 7 were characterized by an almost complete disappearance of algae.

In test no. 3 the wind effect was simulated with a mechanical surface mixer, as compared with the air jets used in all the other tests. For the reasons explained in Section 3.1, the use of this mechanical surface mixer was accompanied with a rise in temperature up to 37°C near the top layers of the pond (Fig. 4.5). The optimum temperature for many green algae is in the order of 30 to 35°C (50, p 56). At temperatures above 35°C the blue-green forms tend to predominate and inhibit the growth of the green forms. This increased temperature provides one explanation for the disappearance of algae observed in test no. 3.

In test no. 7, the observed sulfide concentrations rose to 9.25 mg/l at the end of the dark period. Palmer (50, p 57) reports a toxic level of 3.9 mg/l of sulfides for most diatoms (Bacilliarophyceae). Similarly, Parker (51) reports the disappearance of algae in sewage lagoons when the sulfide concentration values increased to 8.4 mg/l. Therefore, the disappearance of algae in test no. 7 may be explained by the high observed sulfide concentration. Normal algae growth was observed when the average sulfide concentration was 4.29 mg/l (test

no. 4) and 6.36 mg/l (test no. 6). Apparently sulfide concentrations of about 6.5 to 8.5 mg/l produce problems.

2. Tests 1, 4, and 7 permitted some interesting comparisons between concentrations of sulfate ion in the influent and sulfide concentrations in the pond. These three tests were made with the same BOD surface load (136 lb BOD/acre/day) and the same detention time (15 days), the only difference being the concentration of sulfate ion in the influent. A linear relation was observed between the average sulfide concentration in the pond and the influent sulfate concentration (Fig. 4.14). The equation expressing this relation is:

$$[S^{=}] = 0.0216 \cdot [SO_4^{=}] \qquad (4.1)$$

It should be noted that, since the three tests were made in ponds with the same depth, a linear relation also exists between the average sulfide concentration and the sulfate surface load:

$$[S^{=}] = 0.046 \cdot [SO_4^{=} \text{ surface load}] \qquad (4.2)$$

where $[S^{=}]$ and $[SO_4^{=}]$ are in mg/l and $[SO_4^{=}$ surface load$]$ in lbs/acre/day. Hutchinson (27) and Ohle (47), in lake studies, also found a linear relation between sulfide production and sulfate concentration.

3. For the purposes of this investigation, test no. 5 can be considered a failure. The plastic coating on the interior wall of the model failed and corrosion began to occur during test no. 5. The iron

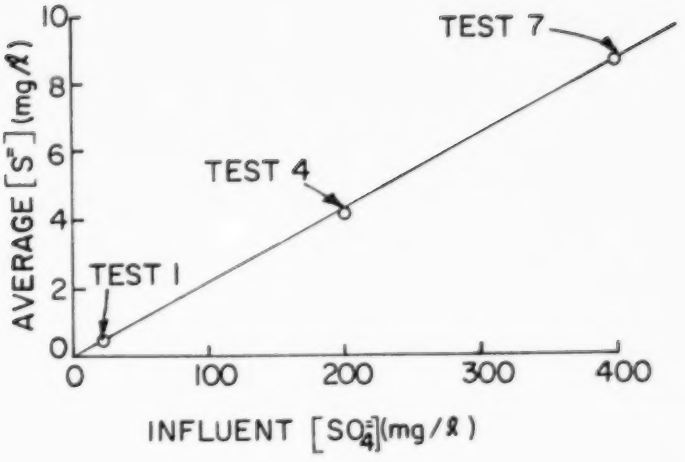



FIG. 4.14 RELATION BETWEEN INFLUENT [$SO_4^=$] CONCENTRATION AND AVERAGE [$S^=$] CONCENTRATION IN THE POND.

concentration in the pond water increased to 3.5 mg/l (as compared with values of 0.2 to 0.3 mg/l observed in the other tests). At this high iron concentration practically all the sulfide precipitated as iron sulfide (FeS). The importance of iron as a catalyst in the oxidation of sulfide was mentioned in Section 2.3. The results of test no. 5 serve to illustrate the point that if the presence of iron is important in the operation of any type of biological treatment,it is particularly important in waste stabilization ponds where odor production may be a problem. The effects of the corrosion observed in this test can be noted by the accompanying high oxidation potentials (Fig. 4.9).

4. The next paragraphs discuss the observed relation between oxidation potentials and sulfide concentrations in the pond.

Since sulfide is a strong reducing agent, the addition of sulfide to the medium is always accompanied by a reduction in the ORP value. This effect, of course, also accompanies the release of sulfide to the medium due to the bacteriological reduction of sulfate. How much the ORP is reduced depends not only on how much sulfide is added, but also on the poisin capacity of the medium, and this poising capacity depends on all the oxidation-reduction reactions that are taking place in the medium. Therefore, a certain amount of sulfide added to the bottom of the pond will have a different effect upon the ORP as compared to a similar amount of sulfide added to the top of the pond. In spite of these different effects, a definite pattern can be observed in

the relation between the ORP and sulfide values measured in the model pond at different depths, and in different experiments (Figs. 4.15 through 4.17).

Figures 4.15 and 4.16 present the ORP-sulfide concentration relationship for tests 1 through 7. In Figs. 4.15 and 4.16, the general pattern followed by the sulfide-ORP relationship is shown with a double line. The results of test no. 6 seem to stand out of the general pattern. This difference may be explained by the fact that in test no. 6 the detention time was 15 days as compared with 30 days used in the other tests shown in the graph. Another reason for this irregularity could be that in test no. 6 the influent BOD was only 37 mg/l, as compared with 74 or 146 mg/l used in the other tests.

The changes in ORP upon addition of different amounts of sulfide to fresh sewage and to sewage prior to a 24-hr anaerobic incubation were experimentally determined by Drynan and Gloyna (16). The results reported by them are similar to the patterns shown in Figs. 4.15 and 4.16. In Fig. 4.17 is presented the same ORP-sulfide relationship. In this case, results reflect an average of the data collected from the top 40 cms of the pond. Here again test no. 6 is out of the general pattern followed by the results of tests no. 1, 2, 4, and 7.

In summary it can be said that small increases in sulfide concentration in the pond will cause large decreases in the oxidation

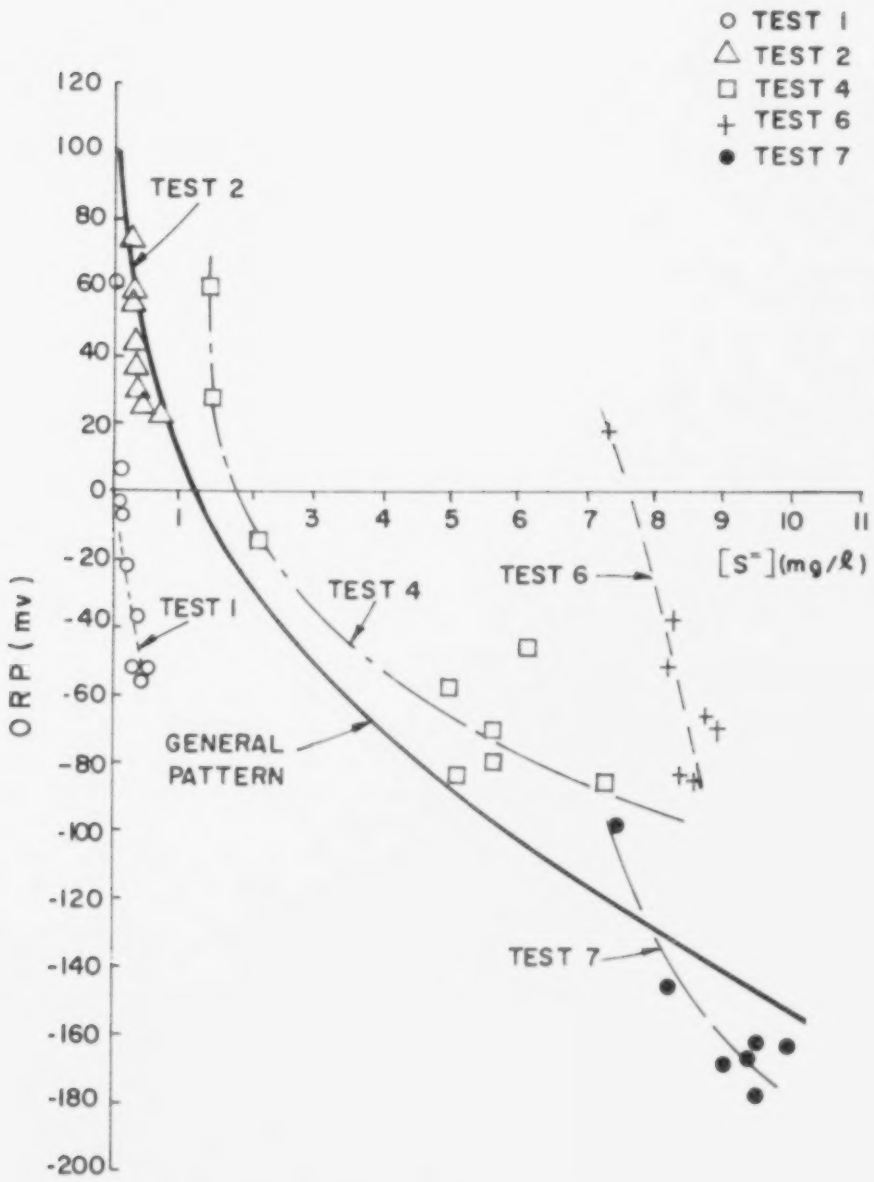



FIG. 4.15. – ORP – [S=] RELATIONSHIPS DURING DARKNESS

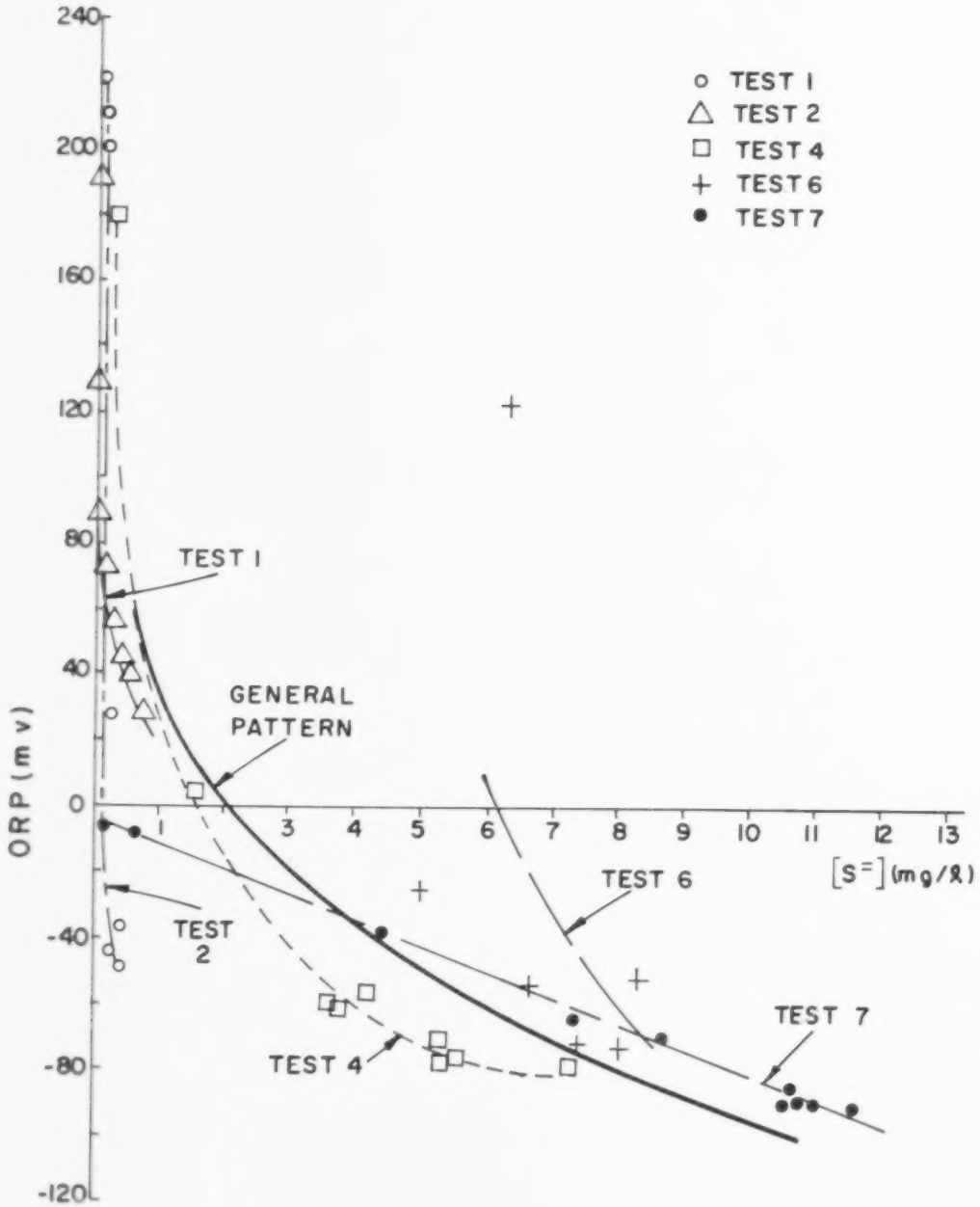



FIG. 4.16.- ORP - [S=] RELATIONSHIPS DURING LIGHT PERIOD

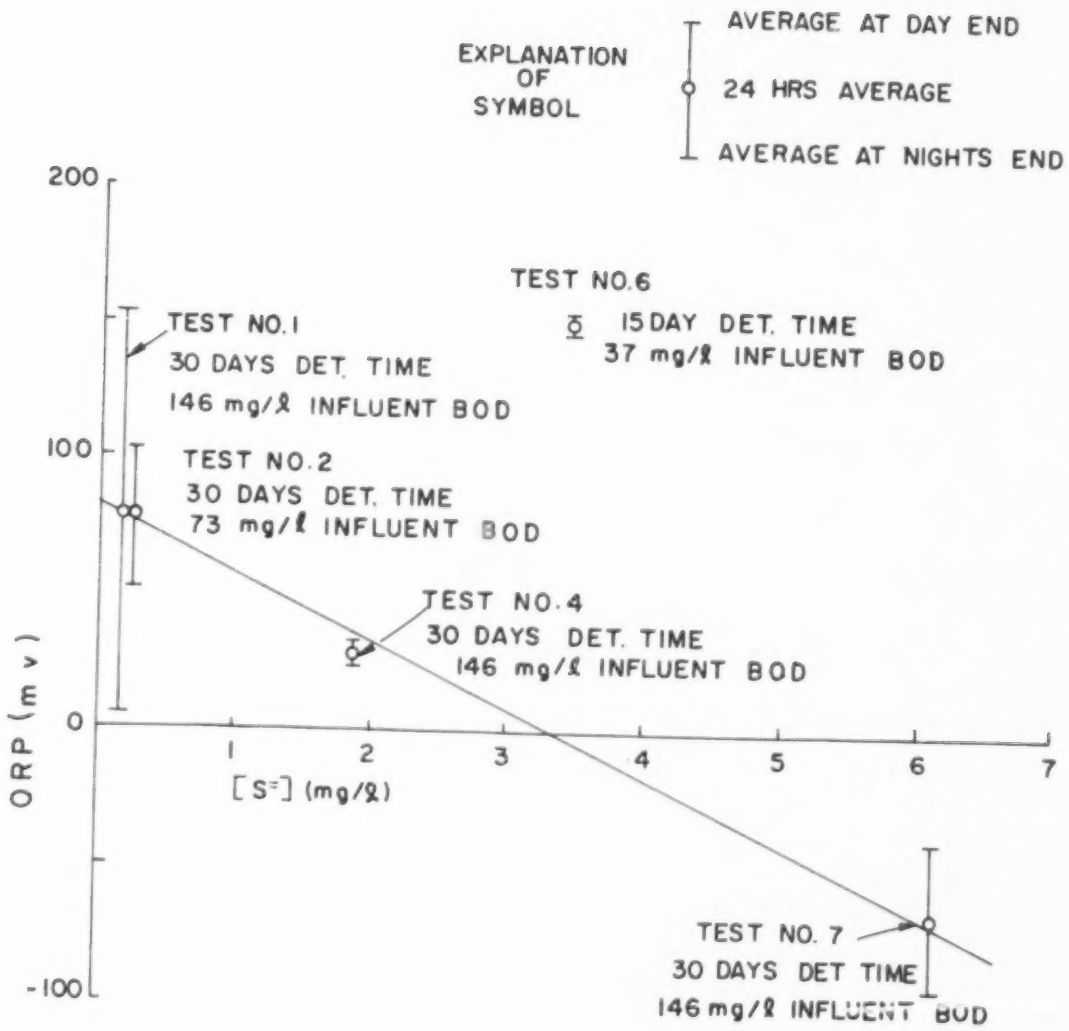



FIG. 4.17. – ORP – [S$^{=}$] RELATIONSHIPS IN TOP 40 cm OF MODEL POND

potential: further increases in sulfide concentration will have smaller effects upon the ORP. The practical application of the above conclusion is that sulfide odor problem in a pond can be detected by ORP controls.

5. During tests no. 4 and 7 determinations were made of the sulfide concentration in the top layers of the pond at different hours of the day. The results of these determinations are presented in Figs. 4.18 and 4.19. The changes of sulfide concentration with time illustrate the importance of the chemical oxidation of sulfide in the pond by photosynthetic oxygen. The changes in sulfide concentration appear as continuous curves with sharp decreases when the lights are turned on and slow increases in concentration after the lights are turned off.

6. A true model, in order to properly simulate the phenomena occurring in an actual waste stabilization pond, must resemble the prototype not only in the physical and hydraulics characteristics, but also, the microbial population of the model must be as similar as possible to the microbial population of the actual pond. While a complete classification of the microorganisms present in the model was beyond the scope of this investigation, microscopic observations provided some valuable information, namely: (a) identification of the predominant algae species and (b) probable identifications of Chromatium and Desulfovibrio.

a. The four groups of algae most commonly found in polluted water are (50): Blue-green algae (Myxophyceae),

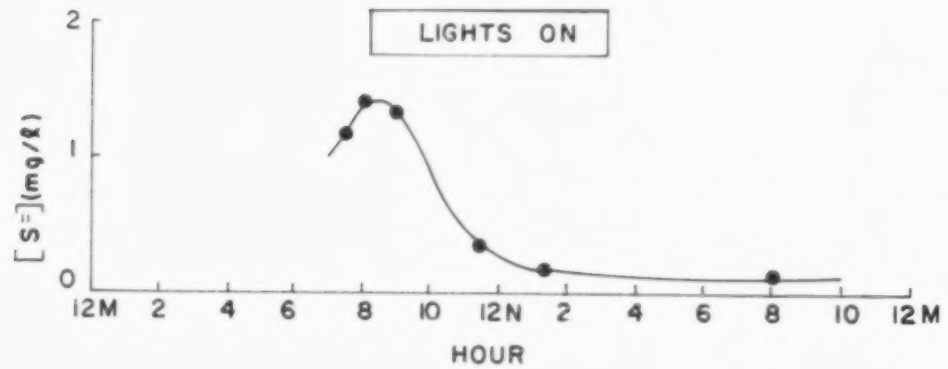



FIG. 4.18. – CHANGE IN [S=] CONCENTRATION IN TOP LAYER DURING THE DAY, TEST NO. 4

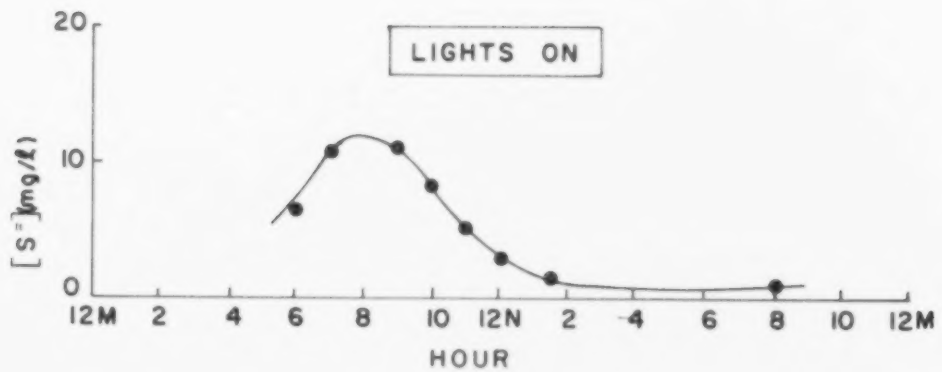
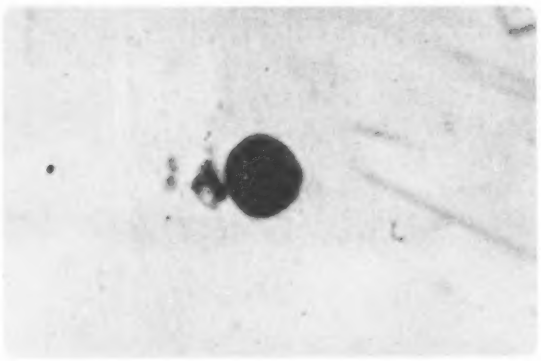



FIG. 4.19. – CHANGE IN [S=] CONCENTRATION IN TOP LAYER DURING THE DAY, TEST NO. 7

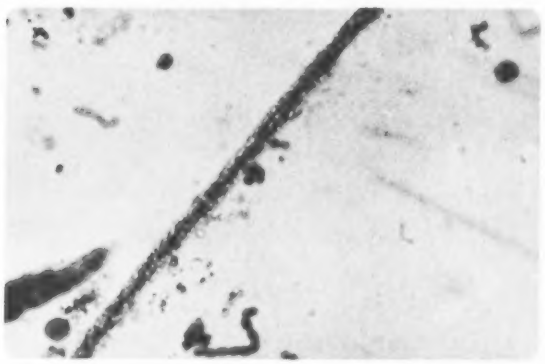
Green algae (non-motile Chlorophyceae), Diatoms (Bacillariophyceae) and Flagellates (Euglenophyceae and Volvocales of Chlorophyceae).

During test no. 4 microscopic observations were made of water taken from the top of the model pond. The predominant algae forms observed were green algae (Chlorella sp.), a flagellate (Chlorogonium sp.) and some unidentified blue-green forms. Photos made of these algal forms are shown in Fig. 4.20. Papenfuss (62) in a systematic study in 1953 of the algae of sewage oxidation ponds in California found that Chlorella and Chlorogonium were the predominant algal species in several cases.

b. Observations using dark-phase technique were made in order to identify Chromatium through their motility and by the presence of sulfur granules stored in the cell, if they are present. These samples were taken at 20 and 40 cm depths during test no. 4. At this time the aerobic layer was 20 cm in depth. Chromatium was not observed; however, Chromatium was identified in samples taken from the feed lines. Part of the feed line consisted of glass tubes that provided excellent conditions of illumination for the growth of photosynthetic bacteria. A typical gram stained smear is shown in Fig. 4.21a. This sample was taken at 20 cm depth during test no. 4.



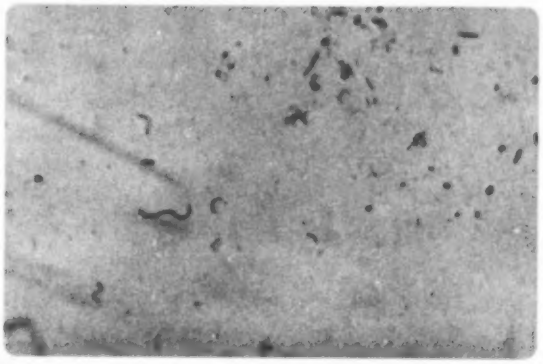
(a) 20 cm deep water sample. Chlorella pyrenoidosa (note chloroplast and pyrenoid).



(b) Top water sample. Unidentified blue-green form.

(c) 20 cm deep water sample. Chlorogonium sp. (note eyespot).

Fig. 4.20 - Predominant Algae Species Found in the Pond Model



(a) 20 cm deep water sample. Gram stained smear. Center-right: probably Athiorodaceae (non-sulfur photosynthetic bacteria); Bottom and bottom left: 3 and 4μ in length rods, probably Chromatium (photosynthetic sulfur bacteria).

(b) 160 cm deep water sample. Gram stained smear. 2μ in length vibrios, probably Desulfovibrio sp.: Center and bottom, probably Lactobacillus sp.

Fig. 4.21 - Some Bacterial Forms Found in Pond Model

Figure 4.21b shows a gram stained smear prepared from pond water taken near the bottom of the model during test no. 4. Some of the forms observed are believed to be Desulfovibrio. Clostridium nigrificans is a rod about 5 $\mu$ in length. Desulfovibrio desulfuricans is a vibrio about 2 $\mu$ in length, both of them belong to the group known as sulfate-reducing bacteria, none of them can be conclusively identified with microscopic observations only.

7. In the next paragraphs the efficiency of the laboratory pond in the removal of organic material is compared with the efficiency that can be expected from an actual pond working under similar conditions.

Table 4.1 presents a summary of the results obtained in the operation of the model pond. The table includes influent BOD, influent COD, average temperature, COD in the pond, percent of COD removed and theoretical efficiency of an actual pond working under similar conditions.

The theoretical efficiencies were computed with the functional relationships developed by Marais, Suwannarkarn and Gloyna (38, 66, 22).

The combined function can be expressed by Eqs. 4.1 through 4.3 (38, p 741 ff):

TABLE 3.1

Summary Of Results at Mixed Pond

| Test Identification and Operation Characteristics | | | | | | | | Results | | | | | | | | | Remarks | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Sulfide Concentration Under Specified Conditions (mg/l) | | | | Average DO Value Under Specified Conditions (mg/l) | | | | | | |
| No. | BOD Load (lb/ac-day) | Infl. $CO_3^{=}$ Conc. (mg/l) | $SO_4$ Load (lb/ac/day) | Det. Time (days) | Infl. $BOD_5$ (mg/l) | Infl. COD (mg/l) | 24 hrs Average Temp. (°C) | At Day's End | At Night's End | 24-hrs Average | In Top 40 cm 24-hrs Aver. | Top 40 cm Day's End | Top 40 cm Night's End | Top 40 cm 24-hrs Aver. | Pond's COD (Average) (mg/l) | Removal Efficiency (%) | Theoretical Efficiency (%) | Device Used For Wind Effect Simulation | Date of Experiment |
| 1 | 136 | 23 | 11 | 30 | 146 | 220 | 21 | 0.374 | 0.491 | 0.432 | 0.265 | +103 | + 3 | + 39 | 78 | 65 | 94 | air jets | Nov., Dec. '66 |
| 2 | 68 | 23 | 11 | 30 | 74 | 110 | 23 | 0.471 | 0.528 | 0.500 | 0.033 | +104 | + 23 | + 38 | 61 | 45 | 93 | air jets | Nov., Dec. '66 |
| 3 | 136 | 23 | 23 | 15 | 292 | 440 | 26.5 | 0.99 | 1.250 | 1.12 | 0.370 | - | - | -- | 76 | 83 | 90 | surface rotator | Sept.,Oct. '66 |
| 4 | 136 | 200 | 94 | 30 | 146 | 220 | 23 | 4.14 | 4.440 | 4.29 | 1.30 | + 32 | + 24 | + 28 | 56 | 75 | 93 | air jets | Jan., Feb. '67 |
| 5 | 68 | 400 | 94 | 60 | 146 | 220 | 28.3 | 0.00 | 0.00 | 0.00 | 0.00 | +215 | +331 | +274 | 58 | 61 | 96 | air jets | Jan., Feb., March '67 |
| 6 | 68 | 200 | 188 | 15 | 37 | 55 | 25 | 6.20 | 6.53 | 6.36 | 3.48 | +152 | +148 | +150 | 32 | 42 | 89 | air jets | March,April '67 |
| 7 | 136 | 400 | 188 | 30 | 146 | 220 | 26 | 8.28 | 9.25 | 8.76 | 6.15 | - 38 | - 94 | - 66 | 37 | 83 | 94 | air jets | May, June '67 |

$$Y_t = \frac{Y}{V/Q} \int_{t=0}^{t=\infty} e^{-K_T t} \cdot e^{-\frac{Q}{V} t} \, dt \qquad (4.1)$$

$$Y_t = \frac{Y}{K_T t + 1} \qquad (4.2)$$

where:

$Y_t$ = Pond and effluent BOD (mg/l)

$Y$ = Influent BOD (mg/l)

$V$ = Volume of the pond

$Q$ = Flow per day

$t$ = Time (days)

$K_T$ = Degradation constant ($days^{-1}$) = $\frac{K_{35^oC}}{(35^oC - T)\theta}$

$\theta$ = Temperature coefficient

$T$ = Temperature ($^oC$)

Marais (38), to test the validity of Eq. 4.2, analyzed results reported by Suwannakarn (66). The experiments of Suwannakarn were conducted on laboratory models of stabilized ponds and used a synthetic substrate similar to the one used in this investigation. The analysis made by Marais yielded values of $K_{35^oC} = 1.2$ $days^{-1}$ and $\theta = 1.085$. The temperature coefficient obtained by Marais is very near to the one (1.072) proposed by Hermann and Gloyna in 1958 (22). To compute the theoretical efficiencies, shown in Table 4.1, Eq. 4.2 was used with the coefficients computed by Marais.

The efficiencies recorded in tests no. 1, 3, 4, 5, and 7 are a little lower than the corresponding theoretical efficiencies. The differences, however, do not seem to be significant. In tests no. 2 and 6, the observed efficiencies are considerably lower than the theoretical efficiencies; but, these differences may be due to the low influent BOD used in both, tests no. 2 and no. 6. The influent BOD in test no. 2 was 75 mg/l and in test no. 6, 37 mg/l.

For practical design, the following equation (Eq. 4.3) can be used (32):

$$V = C \cdot N_p \cdot q \cdot L_a \left[\theta^{(35-T)}\right] f \qquad (4.3)$$

where:

$V$ = pond volume (ac-ft)

$N_p$ = number of people served

$q$ = influent flow (gals/person/day)

$L_a$ = ultimate influent BOD (mg/l)

$\theta$ = temperature coefficient

$T$ = average temperature of the coldest month ($^{o}$C)

$C$ = $10.7 \times 10^{-8}$ (for Hermann-Gloyna formulation, used where temperature fluctuations are large and design based on 6-feet deep ponds)

or $5.37 \times 10^{-8}$ (used where temperature fluctuations

are minimum and where solid accumulation is minimum, suitable for hot, humid tropics. Depth is about 3.5 feet.)

f = algal toxicity factor, the significance of this factor is discussed in detail in (5).

This equation (Eq. 4.3) will be used in the design example presented in the next chapter to illustrate how considerations of sulfide concentrations in the pond will affect a pond design.

The computation of the coefficients of each equation required the results of four different tests. Test no. 5 is one of the four required tests for one of the equations, namely (Eq. type C, Section 3.1):

$$[S^{=}] = a[\text{BOD surface load}] + b[\text{influent } SO_4 \text{ concentration}] + c[SO_4 \text{ surface load}] + d \qquad (4.4)$$

Due to the failure of test no. 5, this particular equation was not developed.

In Section 3.1 the independent variable was broadly defined as "hydrogen sulfide concentration in the pond". The four parameters that were considered to best characterize the problem of sulfides in a pond were: (1) "average-minimum concentration", i.e., average concentration of sulfide in the pond at the end of the light period,

(2) "average-maximum concentration", i.e., average sulfide concentration at the end of the dark period, (3) "24-hours average sulfide concentration in the pond", i.e., the average of (1) and (2) above, and (4) 24-hours average sulfide concentration in the top 40 cm of the pond.

The values of these four parameters are shown in Table 4.1. The data are presented in Tables 4 through 17 in the Appendix.

The general form of the first type of empirical equation to be developed is:

$$[S^{=}] = a[\text{BOD surface load}] + b[SO_4 \text{ influent concentration}] + c[\text{detention time}] + d \qquad (4.5)$$

where $[S^{=}]$ can stand for any of the four mentioned parameters that characterize the problem of sulfides in the pond. The coefficients of the equations of this type were computed with the results of tests no. 2, 3, 4 and 6 (Section 3.1).

Next will be shown the computation of the four coefficients (a, b, c, and d) for the case of $[S^{=}]$ equal to "average-minimum sulfide concentration in the pond".

Substituting the values obtained from test no. 2 into Eq. 4.5, the following are obtained.

$$0.471 \text{ mg/l} = a(68 \text{ lb/acre/day}) + b(23 \text{ mg/l}) + c(30 \text{ days}) + d \qquad (4.6)$$

and similarly with tests no. 3, 4, and 6:

$$0.99 \text{ mg/l} = a(136 \text{ lb/acre/day}) + b(200 \text{ mg/l}) + c(15 \text{ days}) + d \qquad (4.7)$$

$$4.14 \text{ mg/l} = a(136 \text{ lb/acre/day}) + b(200 \text{ mg/l}) + c(30 \text{ days}) + d \qquad (4.8)$$

$$6.20 \text{ mg/l} = a(68 \text{ lb/acre/day}) + b(200 \text{ mg/l}) + c(15 \text{ days}) + d \qquad (4.9)$$

Equations 4.6 through 4.9 can be solved as four simultaneous equations with four incognits (a, b, c, and d). The results are:

$$a = -0.01125 \frac{\text{mg/l}}{\text{lb/acre/day}}$$

$$b = 0.0251 \frac{\text{mg/l}}{\text{mg/l}}$$

$$c = -0.1015 \frac{\text{mg/l}}{\text{day}}$$

$$d = +3.624 \text{ mg/l}$$

The accuracy of the equation so obtained can be checked with the resuits of the two tests that were not used in the development of the equation. For example, the "day's end" sulfide concentration recorded in test no. 7 is 8.28 mg/l and the value computed with Eq. 4.5 is:

$$[S^=] = -0.01125[136] + 0.0251[400] - 0.1015[30] + 3.624$$

$$= 9.08 \text{ mg/l}$$

In Table 4.2 are presented the values of the coefficients a, b, c, and d of Eq. 4.5 for the four different parameters. The table also includes a check on the accuracy and the range of application of the equations.

The second type of equation is of the form:

$$[S^{=}] = a'[\text{BOD surface load}] + b'[SO_4 \text{ surface load}] + c'[\text{detention time}] + d' \qquad (4.10)$$

The coefficients a', b', c', and d' were computed with the results of tests no. 2, 3, 6, and 7 (Section 3.1), and also for the four meanings of $(S^{=})$. The values of the computed coefficients are shown in Table 4.3. In this table, the actual results obtained in tests no. 1 and 4 are compared with the results that would be obtained using Eq. 4.10.

The results obtained suggested that the concentration of sulfide in a pond could be better described by Eqs. 4.11 and 4.12:

$$[S^{=}] = K[SO_4^{=}] \qquad (4.11)$$

$$K = a(\text{BOD surface load}) + b(\text{detention time}) + c \qquad (4.12)$$

where:

$[S^{=}]$ = 24-hrs average sulfide concentration

$[SO_4^{=}]$ = sulfate influent concentration

The coefficients a, b, and c were computed upon the results of the tests made in the model. The method employing the "minimum

TABLE 4.2

Coefficients Equation Type 1

| Values of $[S^{=}]$ (mg/l) | Coefficients | | | | Checks | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Test 1 | | Test 7 | |
| | a | b | c | d | Computed (mg/l) | Recorded (mg/l) | Computed (mg/l) | Recorded (mg/l) |
| (1) Sulfides concentration at day's end | -0.01125 | 0.0251 | -0.1015 | 3.624 | -0.472 | 0.374 | 9.08 | 8.28 |
| (2) Sulfides concentration at night's end | -0.0100 | 0.0259 | -0.0665 | +3.024 | 0.252 | 0.491 | 10.02 | 9.25 |
| (3) 24-hrs average sulfides concentration | -0.01065 | 0.0255 | -0.0895 | +3.324 | -0.182 | 0.432 | 9.39 | 8.76 |
| (4) 24-hrs average sulfides concentration in top 40 cm of pond | -0.00749 | 0.01243 | -0.0714 | +2.574 | -0.2985 | 0.205 | 6.313 | 6.15 |

Remarks: Form of equation: $[S^{=}] = a[\text{BOD surface load}] + b[SO_4 \text{ influent concentration}] + c[\text{detention time}] + d$

The units and range of application of this equation are:
- $[S^{=}]$ in mg/l
- [BOD surface load] in lbs/acre/day; 68 to 136
- $(SO_4)$ influent concentration] in mg/l; 23 to 200
- [detention time] in days; 15 to 30

Characteristics of Test 1 - BOD surface load = 136 lb/acre/day, $SO_4$ influent concentration = 23 mg/l, detention time = 30 days

Characteristics of Test 7 - BOD surface load = 136 lb/acre/day, $SO_4$ influent concentration = 400 mg/l, detention time = 30 days

TABLE 4.3

Coefficients Equation Type 2

| Values of $[S^{=}]$ (mg/l) | Coefficients | | | | Checks | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Test 1 | | Test 4 | |
| | a' | b' | c' | d' | Computed (mg/l) | Recorded (mg/l) | Computed (mg/l) | Recorded (mg/l) |
| (1) Sulfides concentration at day's end | 0.01600 | 0.0379 | 0.0679 | -3.072 | 1.528 | 0.374 | 4.67 | 4.14 |
| (2) Sulfides concentration at night's end | 0.02105 | 0.0411 | 0.0825 | -3.80 | 1.992 | 0.491 | 5.4 | 4.44 |
| (3) 24-hrs average sulfides concentration | 0.01870 | 0.0395 | 0.0752 | -3.436 | 1.76 | 0.432 | 5.035 | 4.29 |
| (4) 24-hrs average sulfides concentration in top 40 cm of pond | 0.02105 | 0.0255 | 0.082 | -3.958 | 1.67 | 0.205 | 3.758 | 1.90 |

Remarks: Form of equation: $[S^{=}] = a'[\text{BOD surface load}] + b'[SO_4 \text{ surface load}] + c'[\text{detention time}] + d'$

The units and range of application of this equation are:
- $[S^{=}]$ in mg/l
- [BOD surface load] in lbs/acre/day; 68 to 136
- [$SO_4$ surface load] in lbs/acre/day; 11 to 188
- [Detention time] in days; 15 to 30

Characteristics of Test 1 - BOD load = 136 lb/acre/day, $SO_4$ load = 11 lbs/acre/day, detention time = 30 days

Characteristics of Test 4 - BOD load = 136 lb/acre/day, $SO_4$ load = 94 lbs/acre/day, detention time = 30 days

square error" was used. The results are as follows:

$$a = 0.0001185 \text{ (lb BOD/acre/day)}^{-1}$$

$$b = -0.001655 \text{ (days)}^{-1}$$

$$c = 0.0553$$

Substituting the derived values of the coefficients into Eqs. 4.11 and 4.12, it is possible to develop Eq. 4.13:

$$[S^{=}] = [0.000185 \cdot (\text{BOD surface load}) - 0.001655 \text{ (detention time)} + 0.0553][SO_4^{=}] \qquad (4.13)$$

Table 4.4 and Fig. 4.22 provide comparisions with the results obtained using Eq. 4.13. The coefficients of Eq. 4.13 were obtained for an average pond temperature of 25°C. It was mentioned before (Section 2.2) that at temperatures below 15°C, the activities of the sulfate-reducing bacteria sharply decrease. Above this temperature the rate of reaction approximately doubles for each 10°C rise. Thus, these temperature effects must be considered when applying Eq. 4.13.

## 4.2 - Hydrogen Sulfide Escaped from Model Pond

Quantitative determinations of hydrogen sulfide were made on the released gases. These determinations were made for 12-, 24- and 48-hour periods during tests no. 4, 6, and 7. The gaseous emissions from the pond were passed through a cadmium sulfate solution (Section

TABLE 4.4

Coefficients Equation 4.13

| Test No. | BOD Surface Load (lb/acre/day) | Detention Time (days) | Influent Sulfate Concentration (mg/l) | K Computed | 24-hrs Average Sulfide Concentration | | K Recorded |
|---|---|---|---|---|---|---|---|
| | | | | | Computed (mg/l) | Recorded (mg/l) | |
| 1 | 136 | 30 | 23 | 0.0218 | 0.500 | 0.432 | 0.0188 |
| 2 | 68 | 30 | 23 | 0.0137 | 0.315 | 0.500 | 0.0217 |
| 3 | 136 | 15 | 23 | 0.0466 | 1.150 | 1.12 | 0.0488 |
| 4 | 136 | 30 | 200 | 0.0218 | 4.36 | 4.29 | 0.0214 |
| 6 | 68 | 15 | 200 | 0.0385 | 7.70 | 6.36 | 0.0317 |
| 7 | 136 | 30 | 400 | 0.0218 | 8.72 | 8.76 | 0.0219 |

Form of equation: $[S^{=}] = K[SO_4^{=}] = [a(\text{BOD load}) + b(\text{detention time}) + c][SO_4^{=}]$

$a = 0.000185$; $b = -0.001655$; $c = 0.0553$

where BOD load - lbs BOD/acre/day
Detention time - detention time in days
$[SO_4^{=}]$ - Influent sulfate concentration (mg/l)

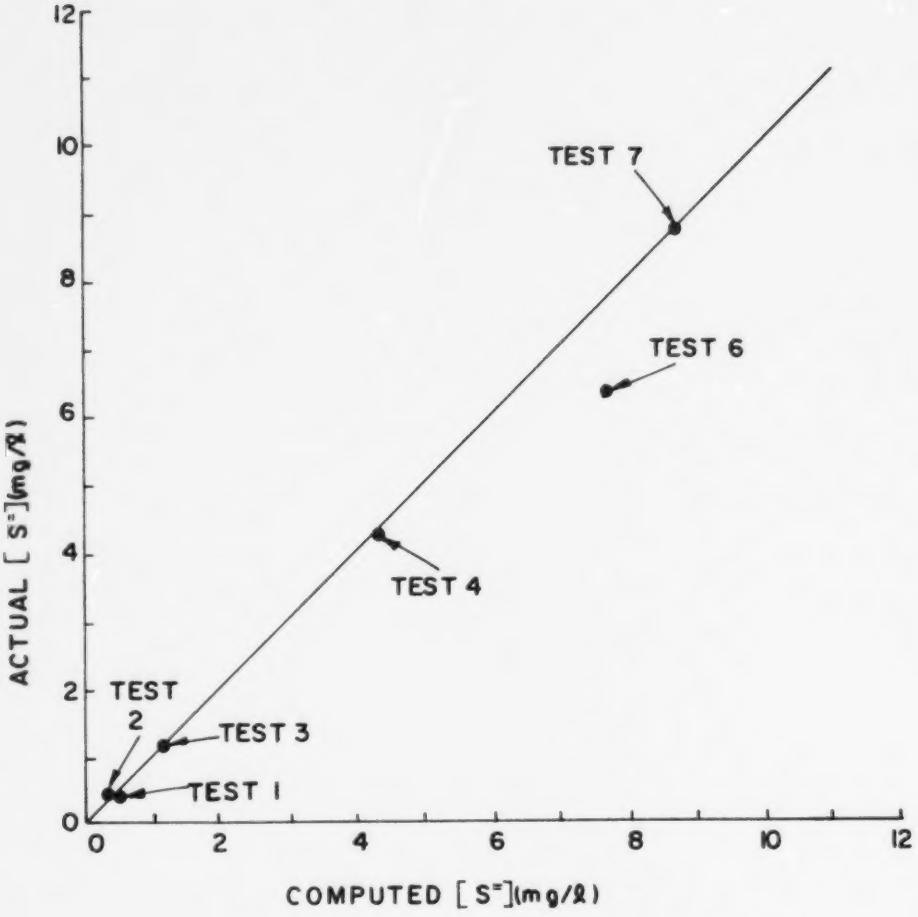



FIG. 4.22.- RESULTS OF EQUATION 4.13

3.2). In the absorbing solution, sulfide precipitates as cadmium sulfide; the amount of sulfide precipitated can be chemically determined.

In none of these experiments could sulfide be detected in the absorbing solution. Apparently, hydrogen sulfide was oxidized either in the surface of the pond or in the surface, probably wetted by the moisture of the air, of the liner conducting the effluent gases to the absorbing solution.

## 4.3 - Exchange of Gases

In this section are presented the results of the infrared analysis of gases exchanged between the model pond and the atmosphere. These analysis were made during test no. 7. The 24-hr. average sulfide concentration in the top 40 cm of the pond was 6.15 mg/l. The sulfide concentration at different hours of the day, near the surface of the pond, are shown in Fig. 4.19.

The moisture of the air samples limited the number of compounds that could be identified by infrared analysis. Figure 4.23 shows the strong absorptions that water has in a large range of the infrared spectrum.

The three gases identified were: methane, hydrogen sulfide, and carbon dioxide. The absorption spectrums of these three compounds are shown in Figs. 4.24(a), 4.24(b), and 4.25.

The methane absorptions at 3000 $cm^{-1}$ in the three different analysis made in this part of the investigation are shown in Fig. 4.26.

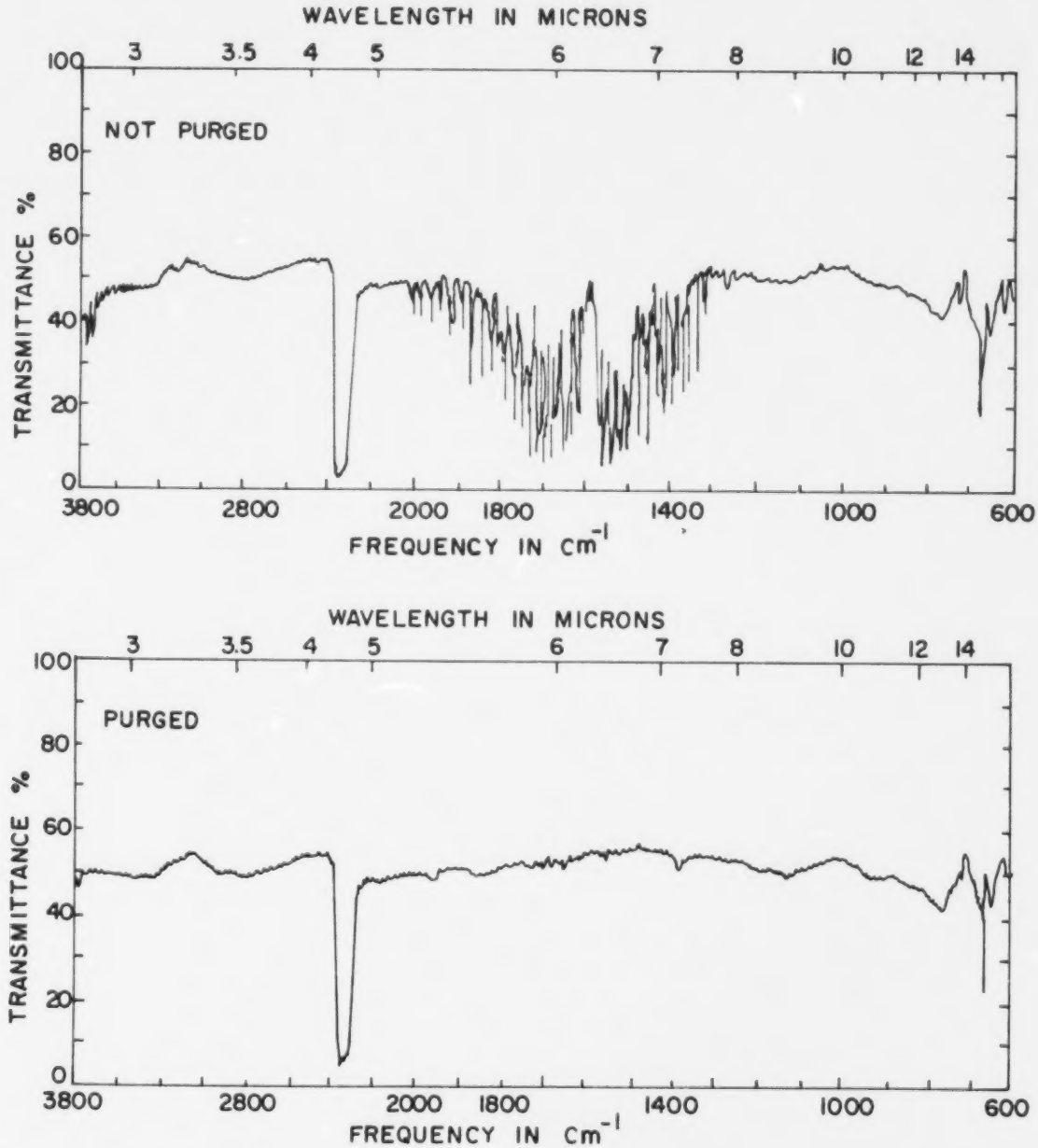



FIG. 4.23. – ABSORPTION SPECTRUM OF AN AIR SAMPLE BEFORE AND AFTER BEING PURGED OF WATER (AFTER (67))

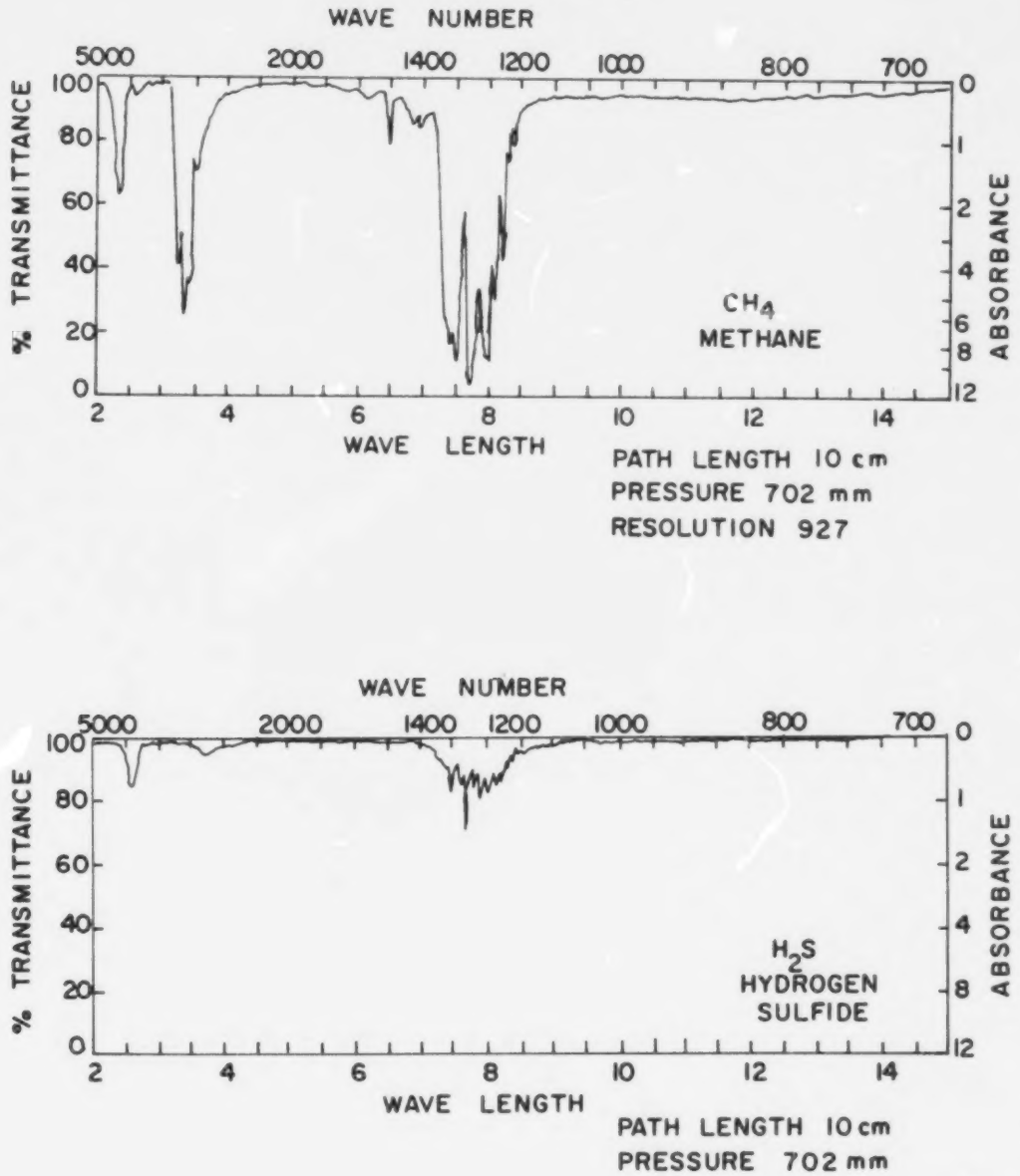



FIG. 4.24.—ABSORPTION SPECTRUMS OF METHANE AND HYDROGEN SULFIDE (AFTER (55))

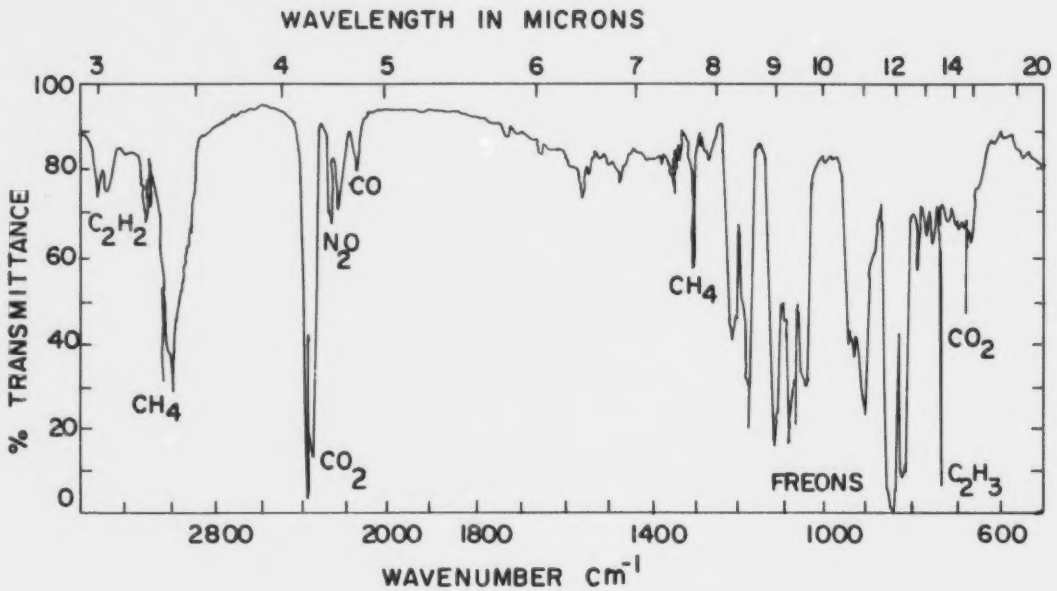



FIG. 4.25.– CALIBRATION SPECTRUM (AFTER(71))

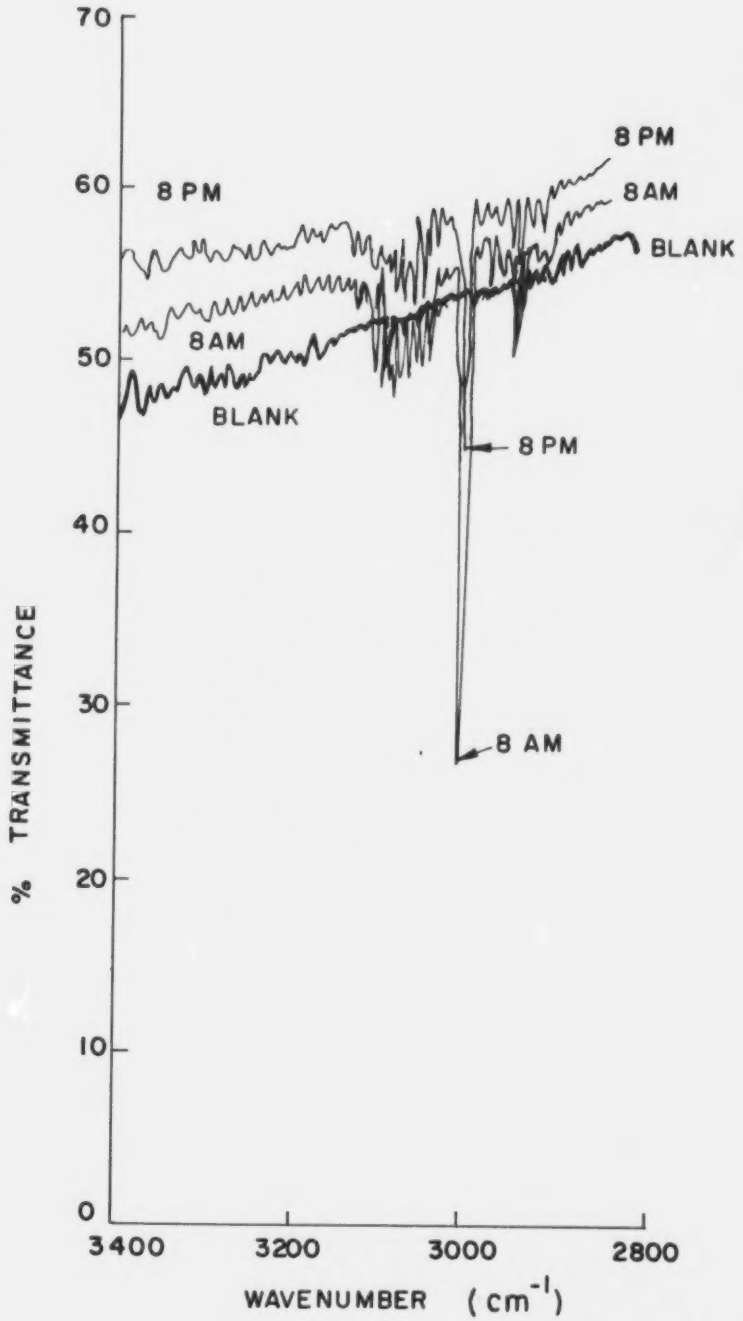



FIG. 4.26.- METHANE ABSORPTIONS

The difference between the "8AM" and the "Blank" samples represents the methane released by the pond during the night. Similarly, the difference between the "8PM" and the "Blank" samples corresponds to the methane released by the pond during the day.

In Fig. 4.27 are shown the absorptions in the 1200 to 1400 $cm^{-1}$ range. The peaks in 1305 $cm^{-1}$ appearing in the "8AM" and "8PM" samples correspond to methane absorptions, confirming what was said before that the pond released methane also during the day. The peak in the "8AM" sample, at about 1295 $cm^{-1}$, is quite probably due to hydrogen sulfide. The "8PM" sample did not present any difference of absorption with the blank at this frequency (1295 $cm^{-1}$). Apparently, hydrogen sulfide was not released by the pond during the day. Two unidentified peaks appeared in the "8AM" sample at about 1330 $cm^{-1}$.

The absorptions corresponding to carbon dioxide are presented in Fig. 4.28. The "8PM" shows a marked reduction in carbon dioxide concentration at the end of the day. This reduction in concentration can be explained by the photosynthetic activities of the algae during the light period. However, the "8AM" sample also shows a reduction in carbon dioxide concentration at the end of the night. This reduction in concentration is probably due to experimental errors. Also, it should be noted that at the end of the day, the water in the top layers might be unsaturated of dissolved carbon dioxide (due to algal

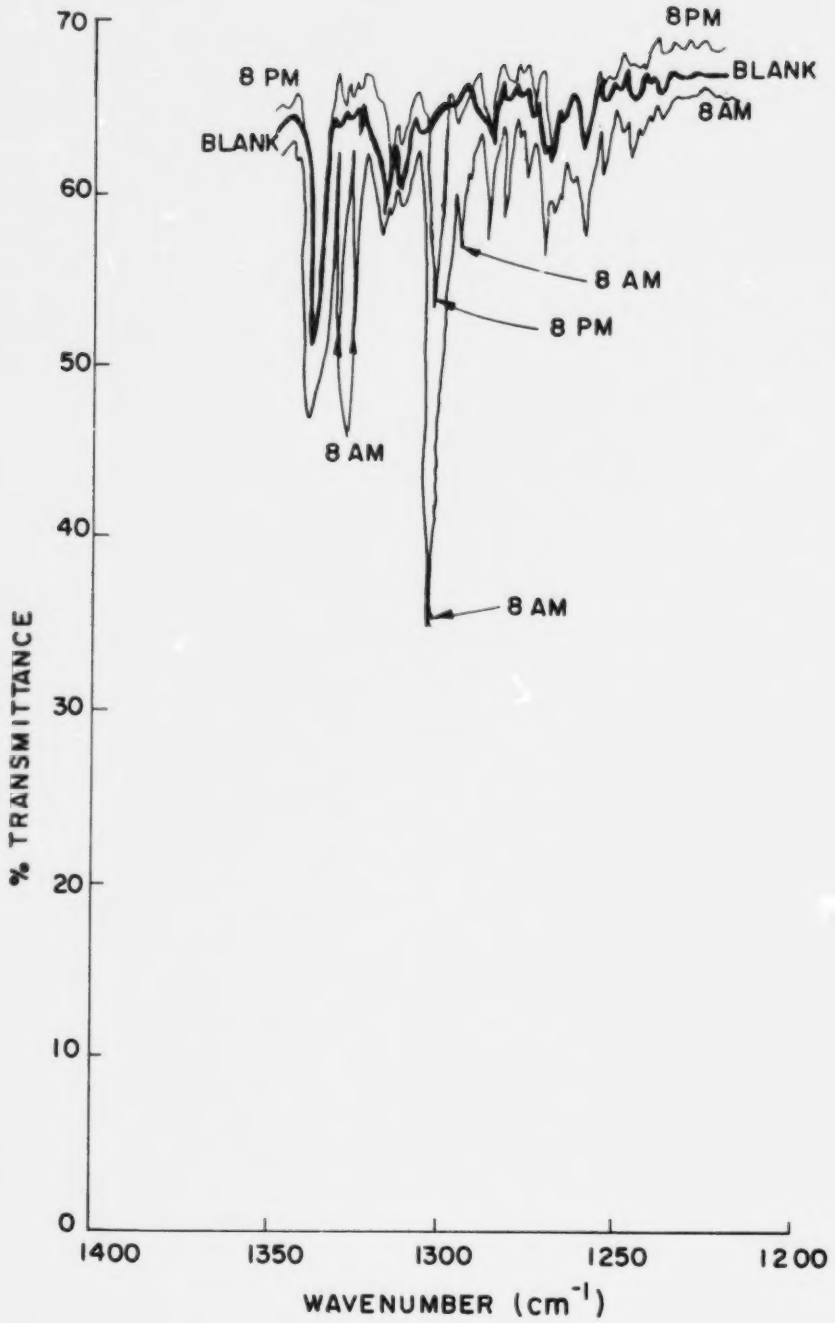



FIG. 4.27. – METHANE AND HYDROGEN SULFIDE ABSORPTIONS

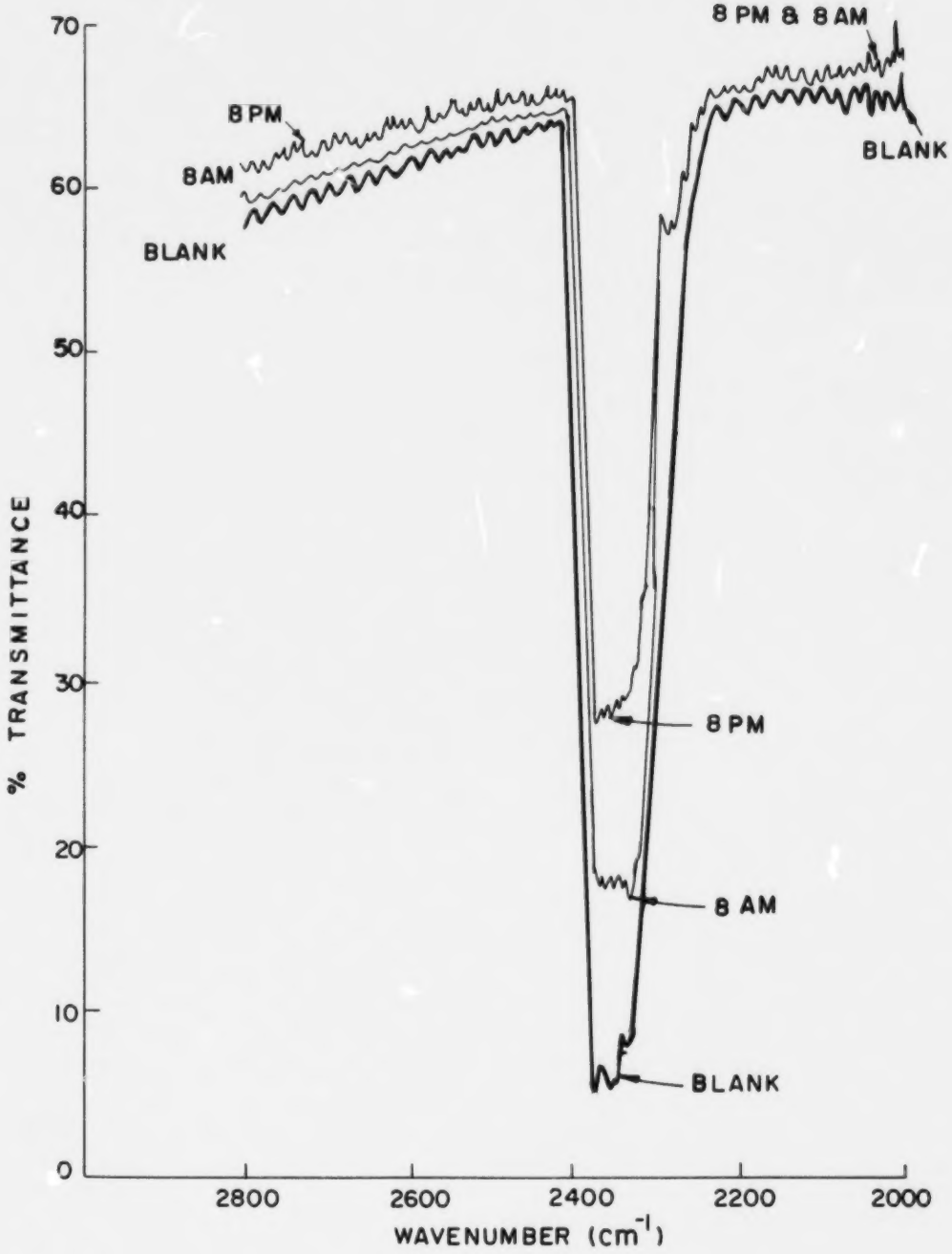



FIG. 4.28. - CARBON DIOXIDE ABSORPTIONS

activity) and some carbon dioxide might diffuse during the night from the air to the pond.

Infrared analysis is useful in the analysis of gaseous emissions from ponds. If the water interference could be eliminated, many more compounds with peaks in the 1200 to 2000 $cm^{-1}$ and 3400 to 4000 $cm^{-1}$ ranges could be identified. Primary and secondary amines with peaks in the 3300 to 3500 $cm^{-1}$ and 1580 to 1650 $cm^{-1}$ ranges fall into this problem area (63, p 69).

## 4.4 - Hydrogen Sulfide Transfer Rates

In this section are presented the results of the experiments undertaken to study the transfer of hydrogen sulfide gas from water to the atmosphere. The presentation of the results is divided into three parts.

The first part deals with the changes in sulfide concentration in a water sample due to chemical oxidation and to transfer of hydrogen sulfide to the atmosphere. The second part deals with an indirect quantification of the effects of chemical oxidation resulting from reaeration. The third part deals with a direct determination of the rate of transfer of hydrogen sulfide gas from water to an atmosphere void of oxygen or any other chemical oxidant.

### Concentration Changes Due to Escape and Chemical Oxidation:

A summary of the characteristics of the tests is presented in Table 4.5.

TABLE 4.5

Summary of Results of Hydrogen Sulfide Transfer Tests

| Test No. | Type of Water Sample | pH | $\frac{H_2S}{[S^=]}$ (%) | Sample Volume (liters) | $\frac{A}{V}$ (1/m) | k (m/hr) | Mixing | Dissolved Oxygen At Time Zero |
|---|---|---|---|---|---|---|---|---|
| 1 | Pond | 7.0 | 47.7 | 3 | 5.5 | 0.0755 | Slow | No |
| 2 | Pond | 7.0 | 47.7 | 3 | 5.5 | 0.110 | Slow | No |
| 3 | Pond | 7.8 | 12.7 | 3 | 5.5 | 0.610 | Slow | No |
| 4 | Distilled | <4.5 | 100 | 3 | 5.5 | 0.00578 | None | Yes |
| 5 | Distilled | <4.5 | 100 | 3 | 5.5 | 0.00644 | None | Yes |
| 6 | Distilled | <4.5 | 100 | 2 | 8.25 | 0.00596 | None | Yes |
| 7 | Distilled | <4.5 | 100 | 2 | 8.25 | 0.00596 | None | Yes |
| 8 | Pond | <4.5 | 100 | 3 | 5.5 | 0.00680 | None | No |
| 9 | Pond | <4.5 | 100 | 2 | 8.25 | 0.00641 | None | No |
| 10 | Pond | <4.5 | 100 | 1 | 16.5 | 0.00664 | None | No |

The table shows that these tests were made using different waters, pH levels and mixing conditions. The water temperature in all these tests was $22 \pm 2^{o}C$. In the first three tests the pH was set at 7.0, 7.0, and 7.8, while in the remaining tests the pH was reduced to 4.5 or less because small fluctuations in pH do not affect the (hydrogen sulfide)/(total sulfide) relationship in the lower range. Initial mixing was provided in all tests, but mixing was continued only during the first three tests.

Results of the first three tests are shown in a semilog plot of hydrogen sulfide concentration (as S) at time t versus $t \cdot \frac{A}{V}$ (Fig. 4.29). The data collected in these, and all the other tests, are presented in Tables 18 through 23 in the Appendix. The containers used provided a surface (A) of 166 $cm^2$ and a volume (V) of 3 L. This gives an A/V relationship of 5.5 $m^{-1}$. During these three tests the pH fluctuated about 0.2 units, possibly due to algal activity. This slight change in pH might affect the sulfides equilibrium reaction (Eqs. 2.11 through 2.14), and consequently, the $(H_2S)/(\text{total } S^{=})$ relationship and the rate of escape.

Distilled water was used in tests four (3 L), five (3 L), six (2L), and seven (2 L). The results for these tests are presented in Figs. 4.30 through 4.33. In all of these tests a sharp decrease in sulfide concentration was observed in the first stages of the experiment.

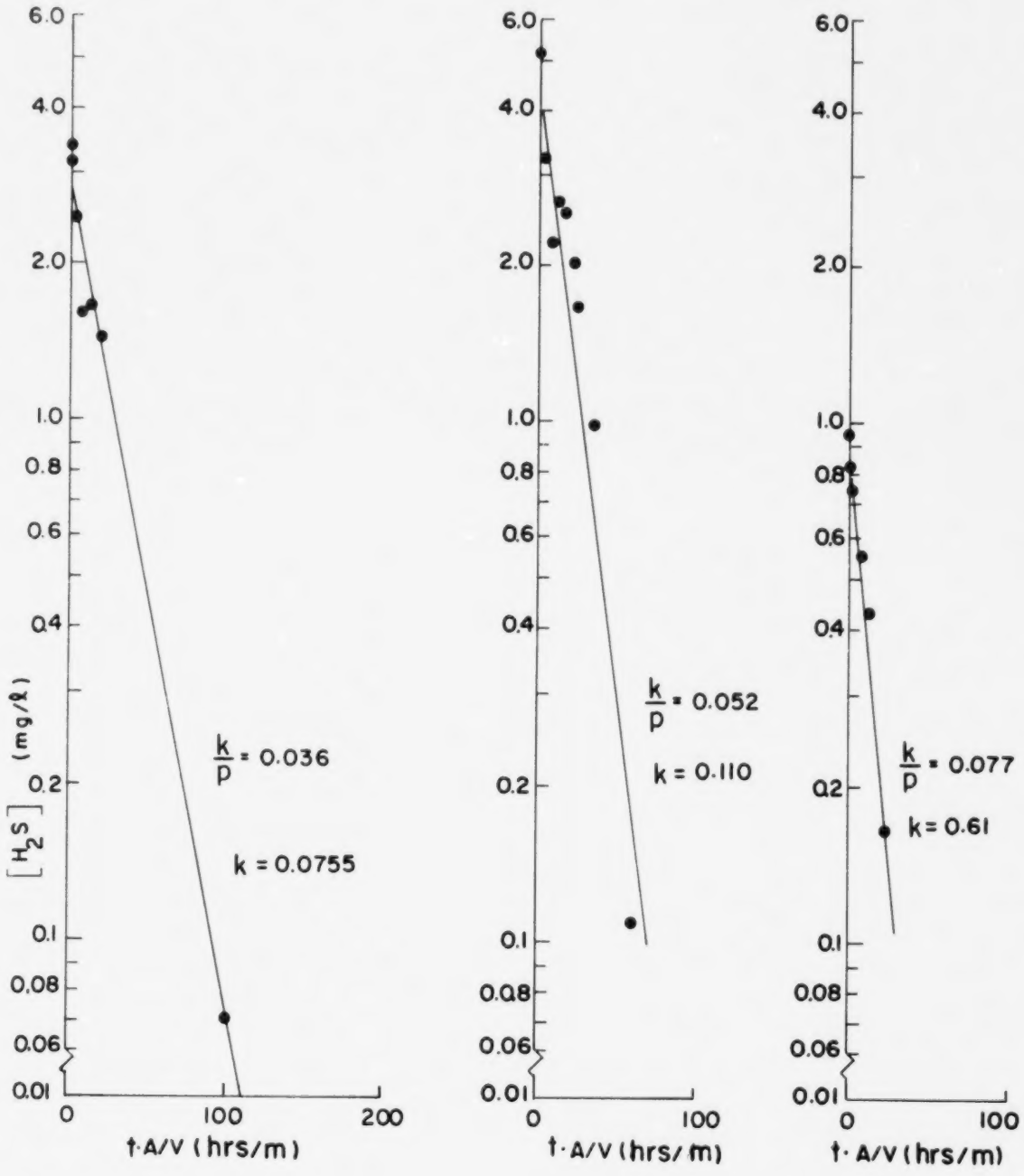



FIG. 4.29. – CHANGES HYDROGEN SULFIDE CONCENTRATION DURING TESTS 1, 2, AND 3.

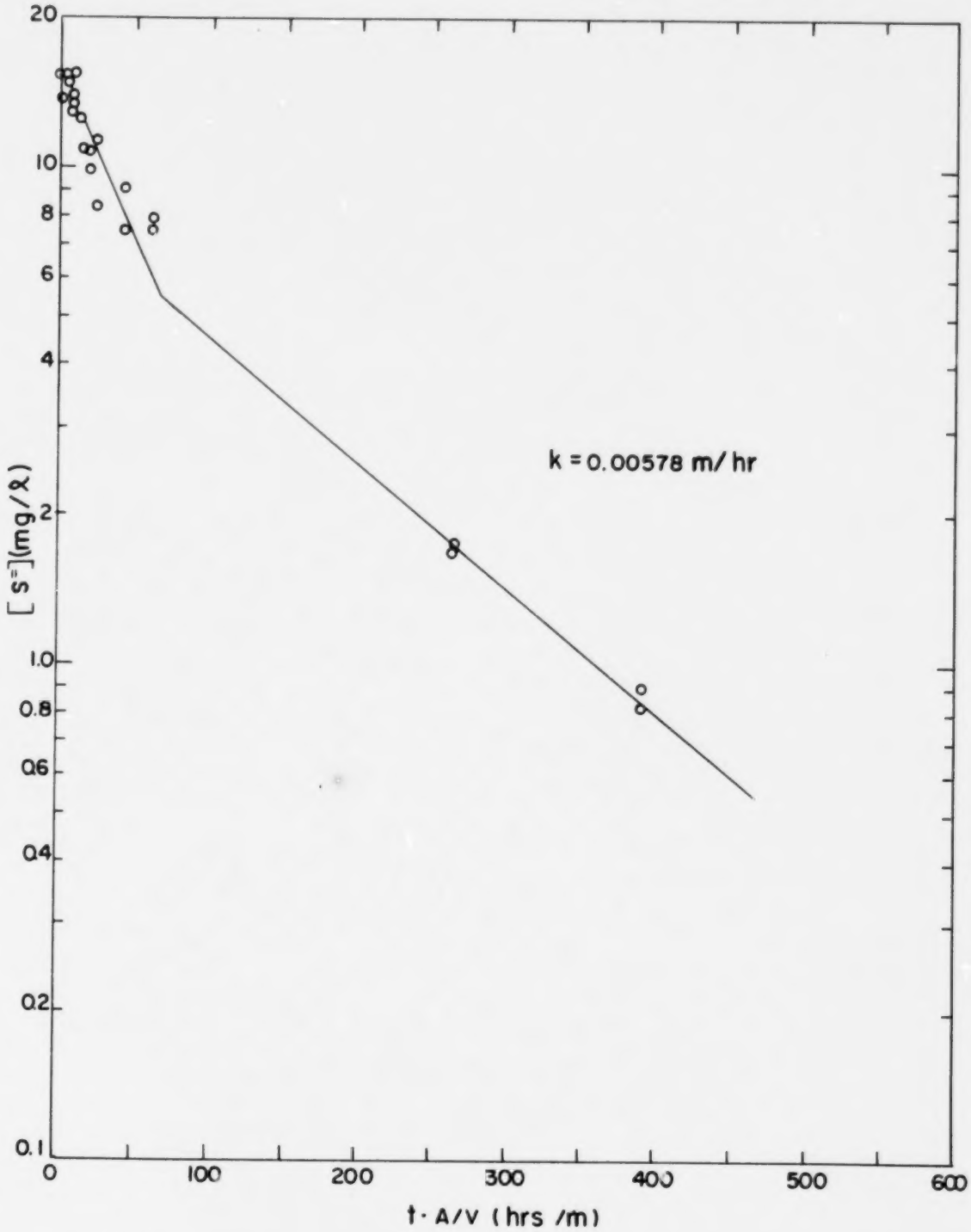



FIG. 4.30.–CHANGES IN SULFIDE CONCENTRATION DURING TEST 4

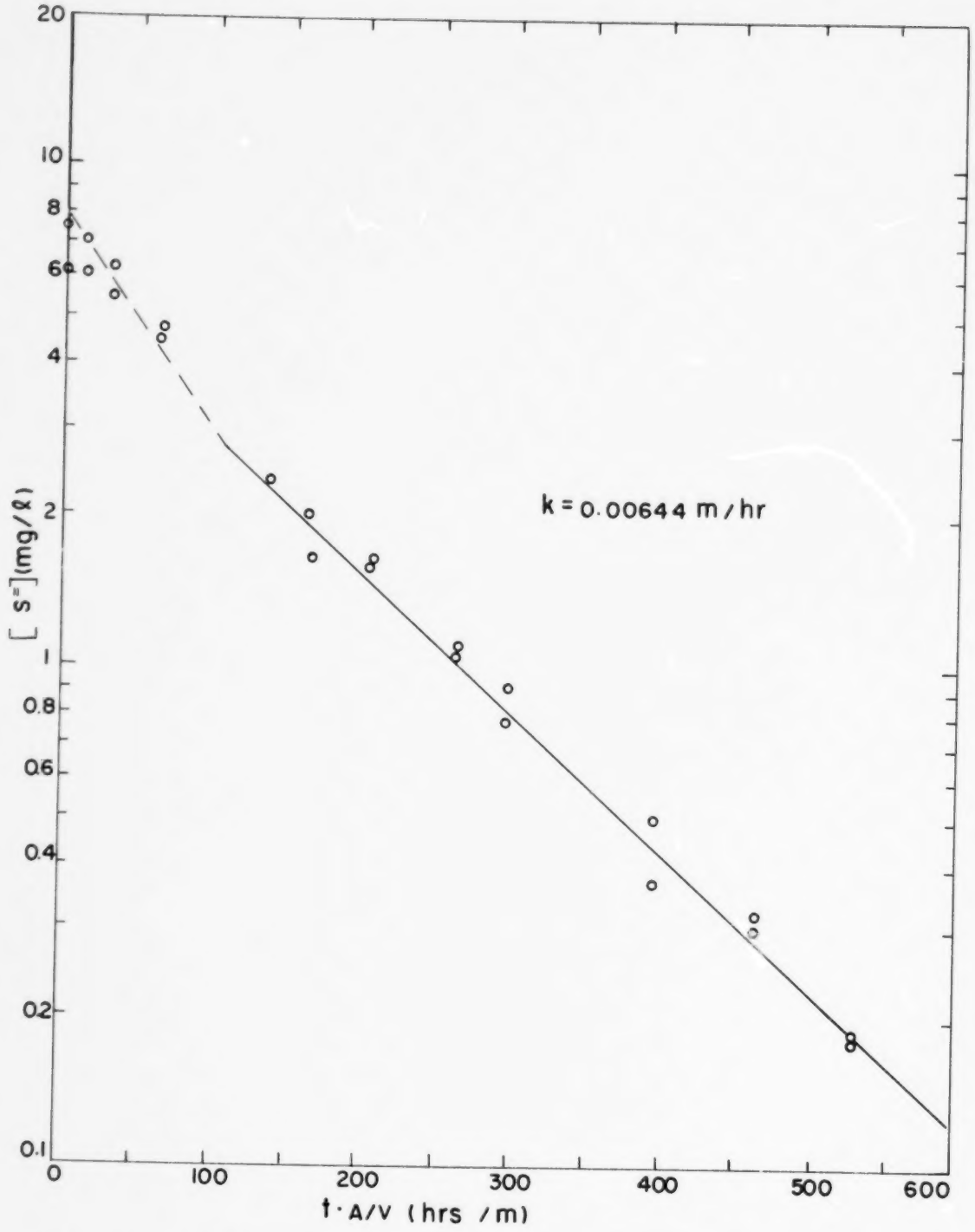



FIG. 4.31.– CHANGES IN SULIFIDE CONCENTRATION DURING TEST 5

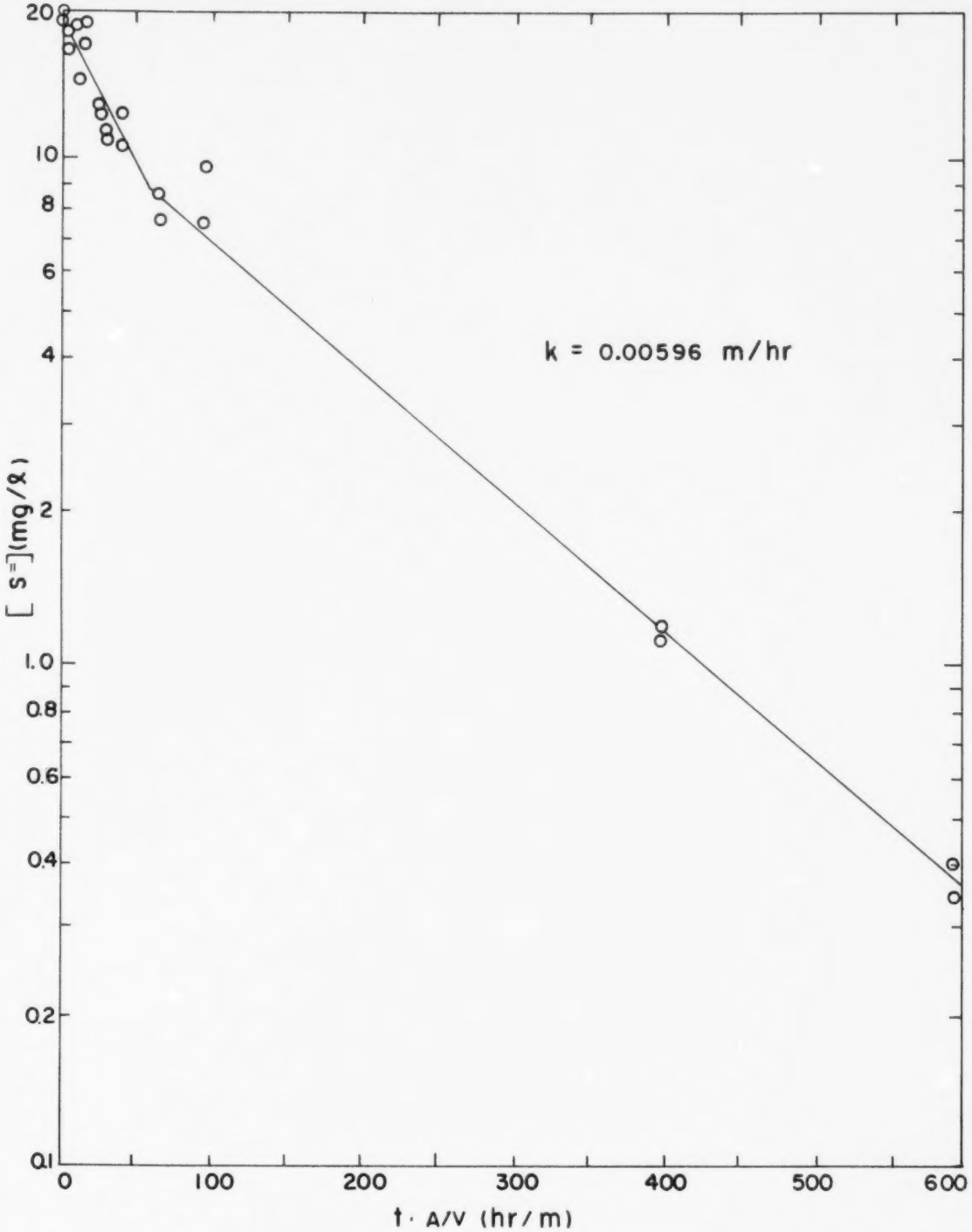



FIG. 4.32.–CHANGES IN SULFIDE CONCENTRATION DURING TEST 6

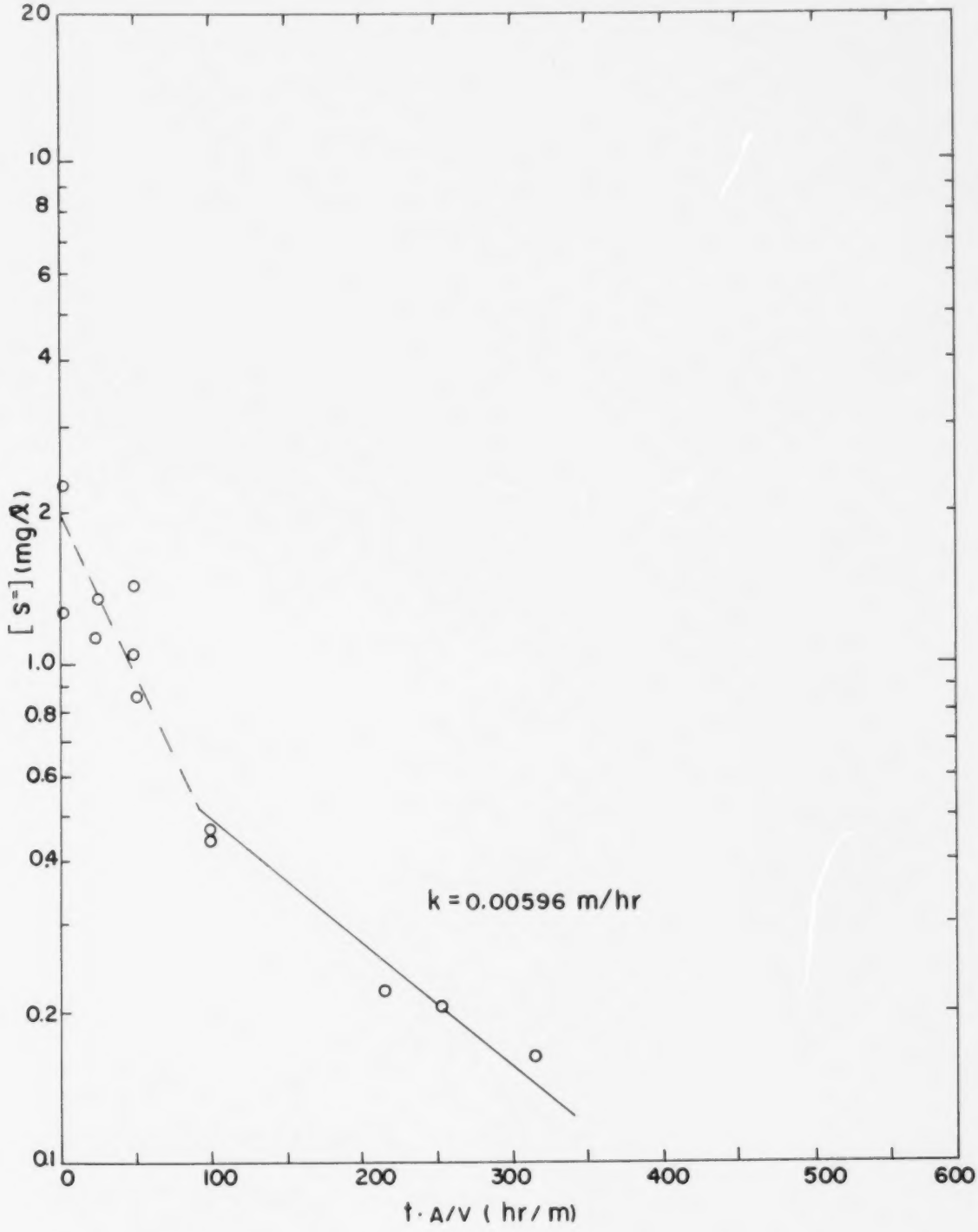



FIG. 4.33.– CHANGES IN SULFIDE CONCENTRATION DURING TEST 7

This decrease is due to the oxidation of sulfide by the dissolved oxygen. However, of more importance is the fact that the decrease in sulfide concentration (after the rapid initial reduction) is a linear function of the logarithm of the concentrations. This linearity, as indicated in Section 3.4, shows that the decrease in concentration is due mostly to hydrogen sulfide release and is affected very little by surface reaeration. The b values shown in Figs. 4.29 through 4.33 were computed on the basis that no oxidation occurred due to reaeration. The k values were very close to each other: 0.0058, 0.0064, 0.0060, and 0.0060 m/hr. For tests one, two and three, respectively, k values were computed on the same basis and were 0.755, 0.110, and 0.610 m/hr. The k values for the first three tests were greater because the stirrer increased the renewal rate of the surface film.

In the next three tests the experiments were repeated using pond water. The pH was set to a value below 4.5. No oxygen was present in the water at the beginning of the tests and the volumes used were three, two, and one liter, respectively, for tests eight, nine and ten. The results are shown in a semilog plot of $[S^{=}]$ versus $t \cdot \frac{A}{V}$ in Figs. 4.34 through 4.36. (At pH below 4.5 all sulfide exists as hydrogen sulfide.) Notably, there was no sharp decrease in sulfide concentration at the beginning of these experiments as compared to tests four through seven. This agrees with the explanation given before; namely, the sharp decrease is due to dissolved oxygen present

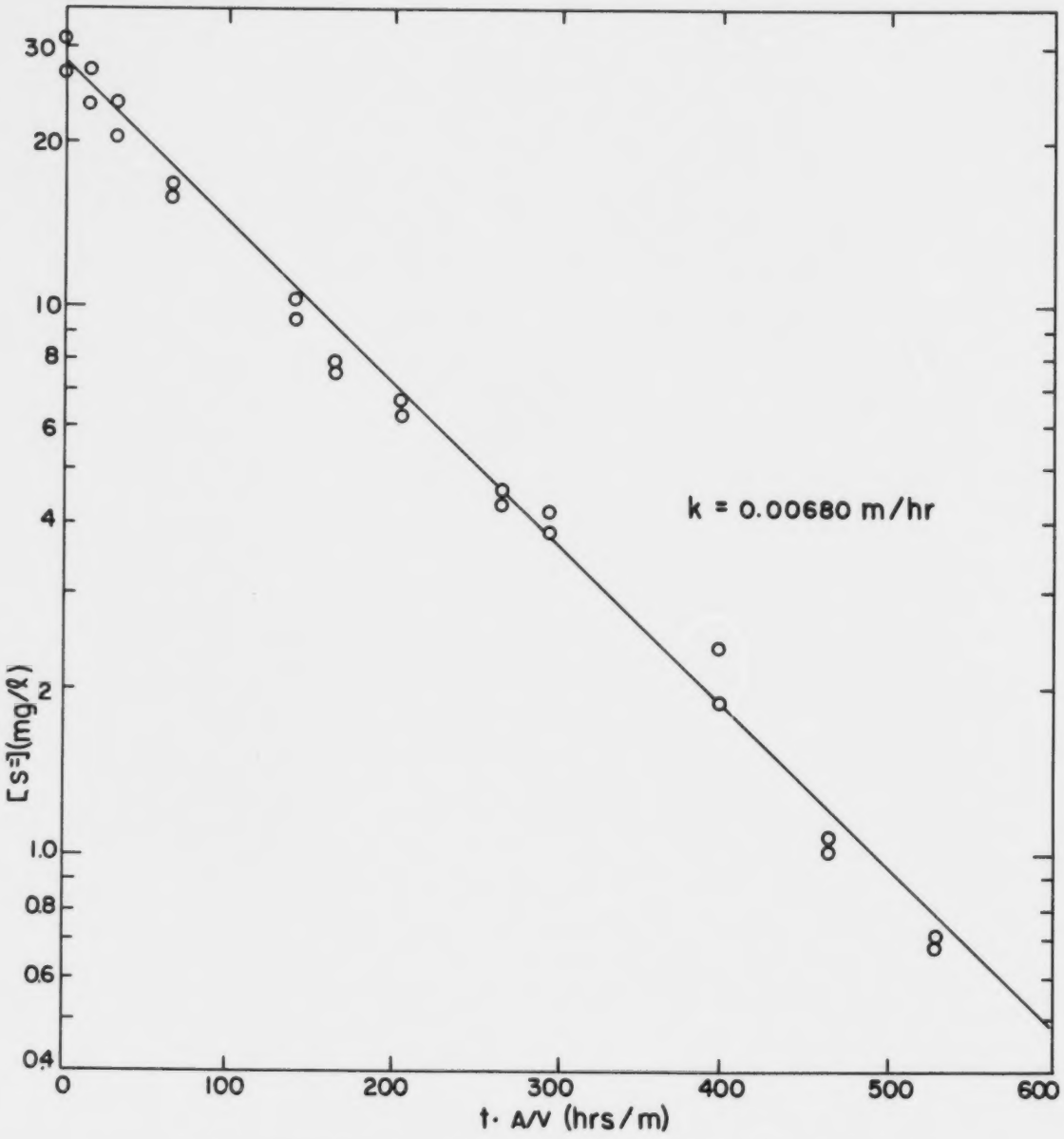



FIG. 4.34.- CHANGES IN SULFIDE CONCENTRATION DURING TEST 8

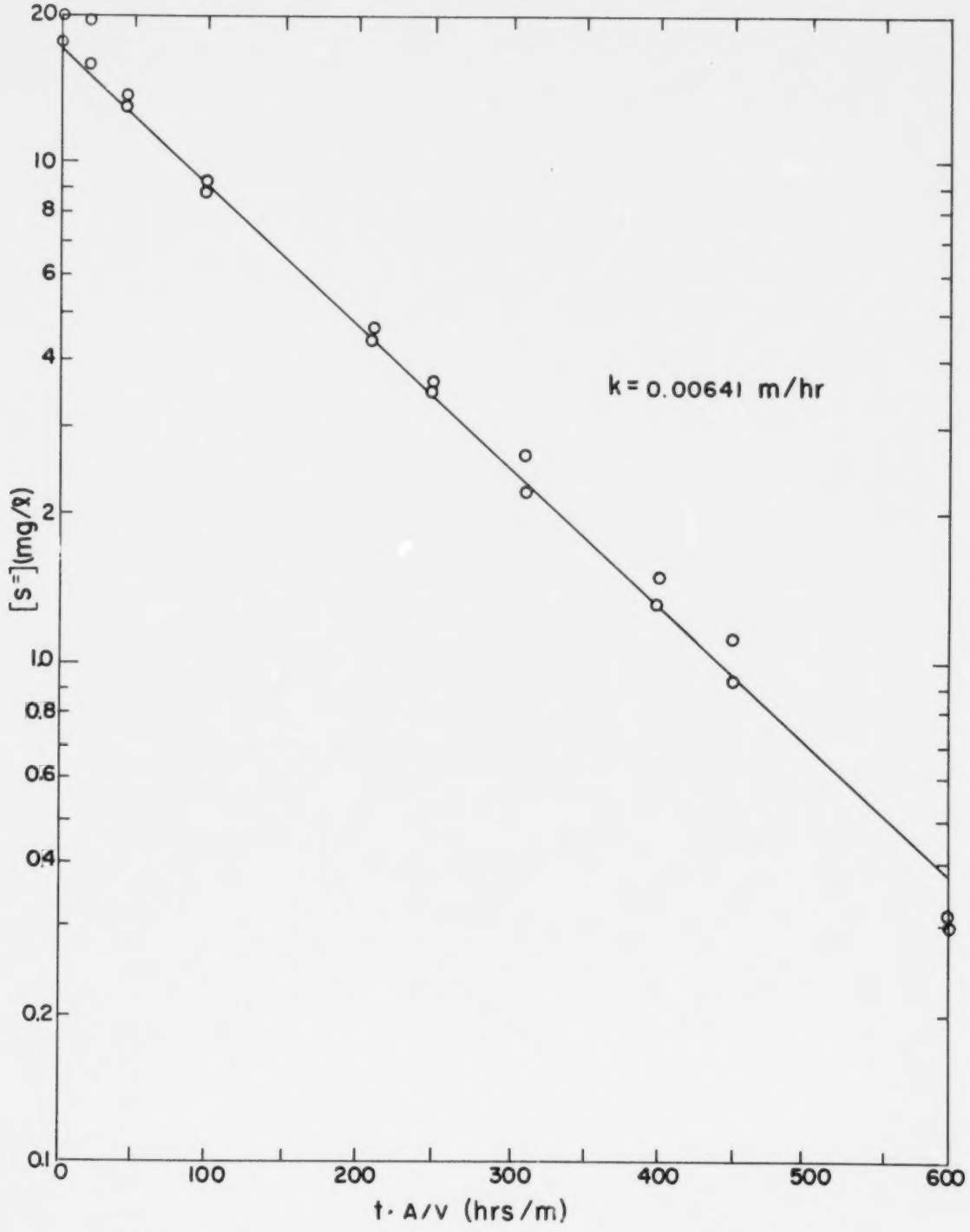



FIG. 4.35.- CHANGES IN SULFIDE CONCENTRATION DURING TEST 9

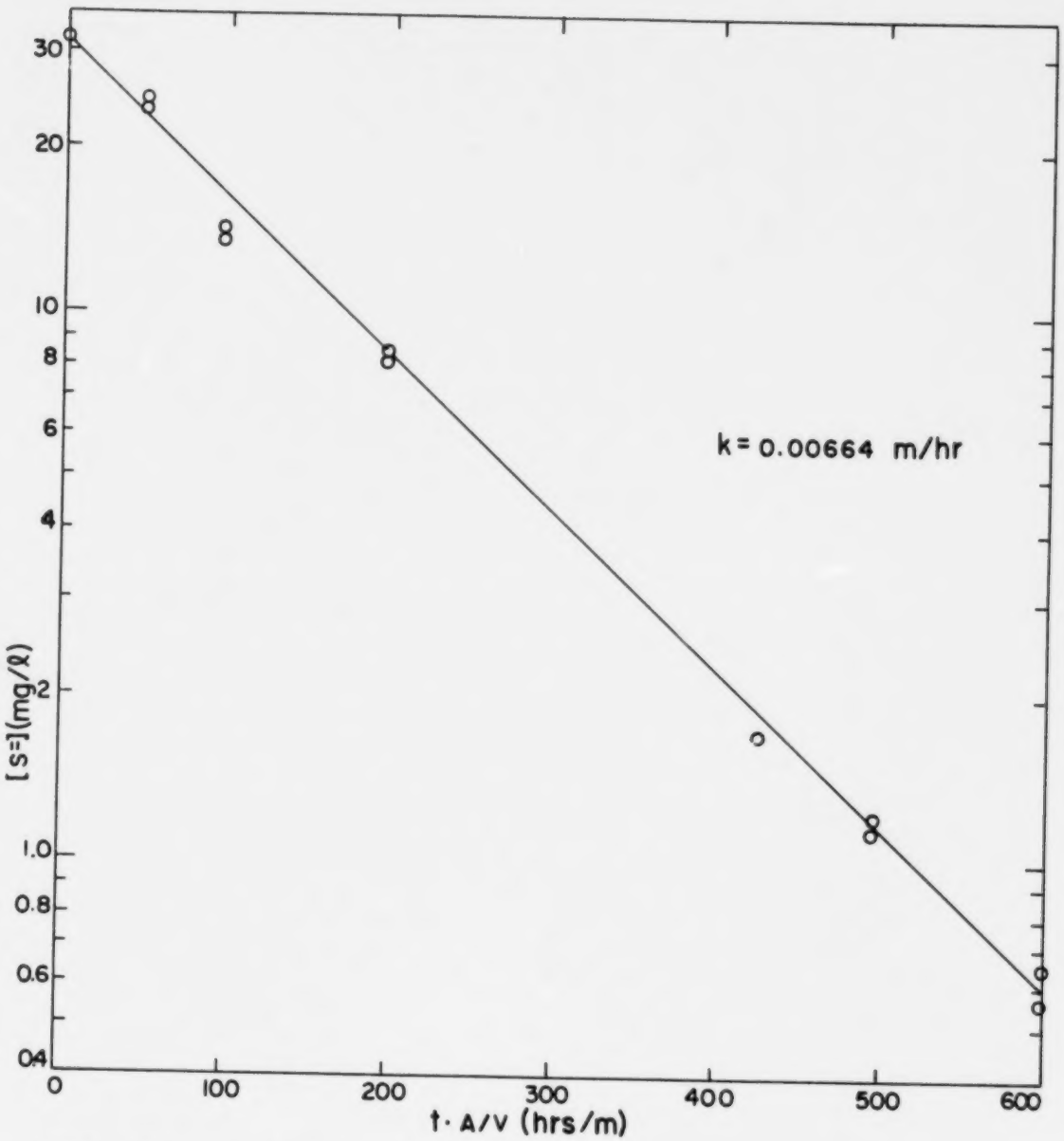



FIG. 4.36.- CHANGES IN SULFIDE CONCENTRATION DURING TEST 10

at the beginning of the test. Again in these latter three tests the decrease in concentration appears as a linear logarithmic function of $t \cdot \frac{A}{V}$. The computed k values are 0.0068, 0.0064, and 0.0066 m/hr. These values are slightly higher than the average k value computed for distilled water under the same conditions (0.00605 m/hr). The difference, however, does not seem to be significant.

The linear logarithmic decrease function observed in the ten tests indicates very little or no importance of reaeration during the experiments. This unimportance of reaeration can be due to either one of the next two reasons, viz.:

a) aeration occurred at such a low rate that the effects were masked by the high hydrogen sulfide escape rates

b) aeration occurred at a rate comparable to the hydrogen sulfide escape rates, but the oxygen provided by reaeration was made unavailable for the oxidation of the sulfides remaining in solution.

To study this question, the reaeration rate was determined using water samples similar to those used in the previous tests. These results are described below.

Oxygen Diffusion Rate: The results of the oxygen diffusion studies are shown in Fig. 4.37. Two tests were made using distilled water, one with two liters and one with three liters. The diffusion

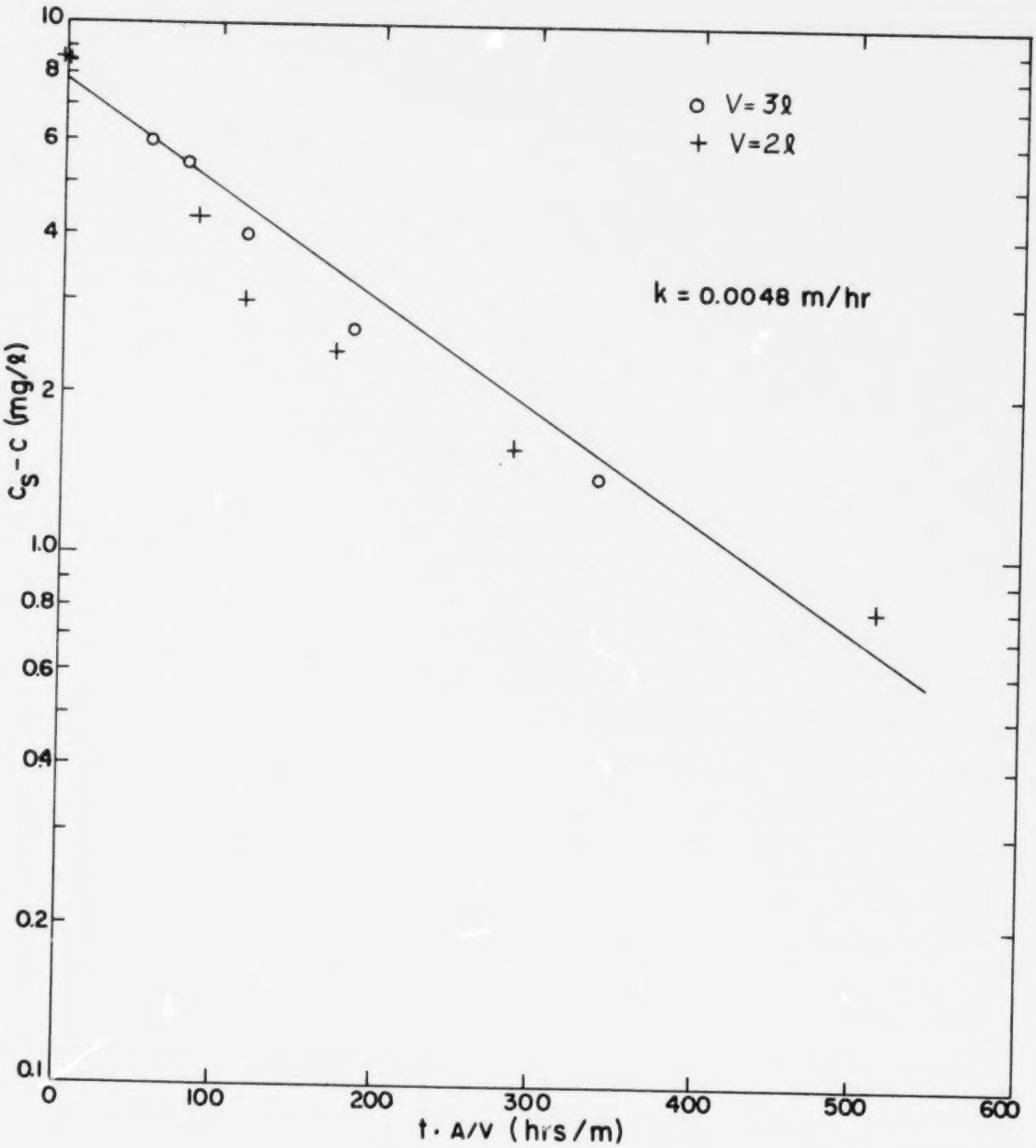



FIG. 4.37. - OXYGEN DIFFUSION IN WATER

constant k computed with the results of these two tests in 0.0048 m/hr. This k value is of the same order of magnitude as the one obtained in tests four to eight (0.00605 m/hr). Consequently, the linear logarithmic decrease observed in tests one through ten was due to reason (b) mentioned before, viz.: the escape of hydrogen sulfide interferred with the diffusion of oxygen or reacted with oxygen in the surface in the surface film. This explanation seems to be confirmed by the null results obtained in the quantitative determinations of hydrogen sulfide gas escaping from the model pond (Sections 3.3 and 4.3). However, in this case, as noted before, the oxidation of the escaping hydrogen sulfide could occur not only in the surface film, but also in the wet surface of the plastic tubes used to transport the effluent gases to the absorbing solution.

Further evidence in favor of the above explanation was given by the results of the next test, where the rate of escape was measured using an oxygen-free atmosphere.

Escape Rate: In this experiment the changes in sulfide concentration were measured in a water sample which was in contact with a carbon dioxide atmosphere. Three liters of distilled water were used in the test, although the container was slightly different from the jars used in the previous experiments. The surface area in contact with the carbon dioxide atmosphere was 188 $cm^2$, giving an A/V relationship of 6.25 $m^{-1}$. The results obtained are shown in Fig. 4.38. At time

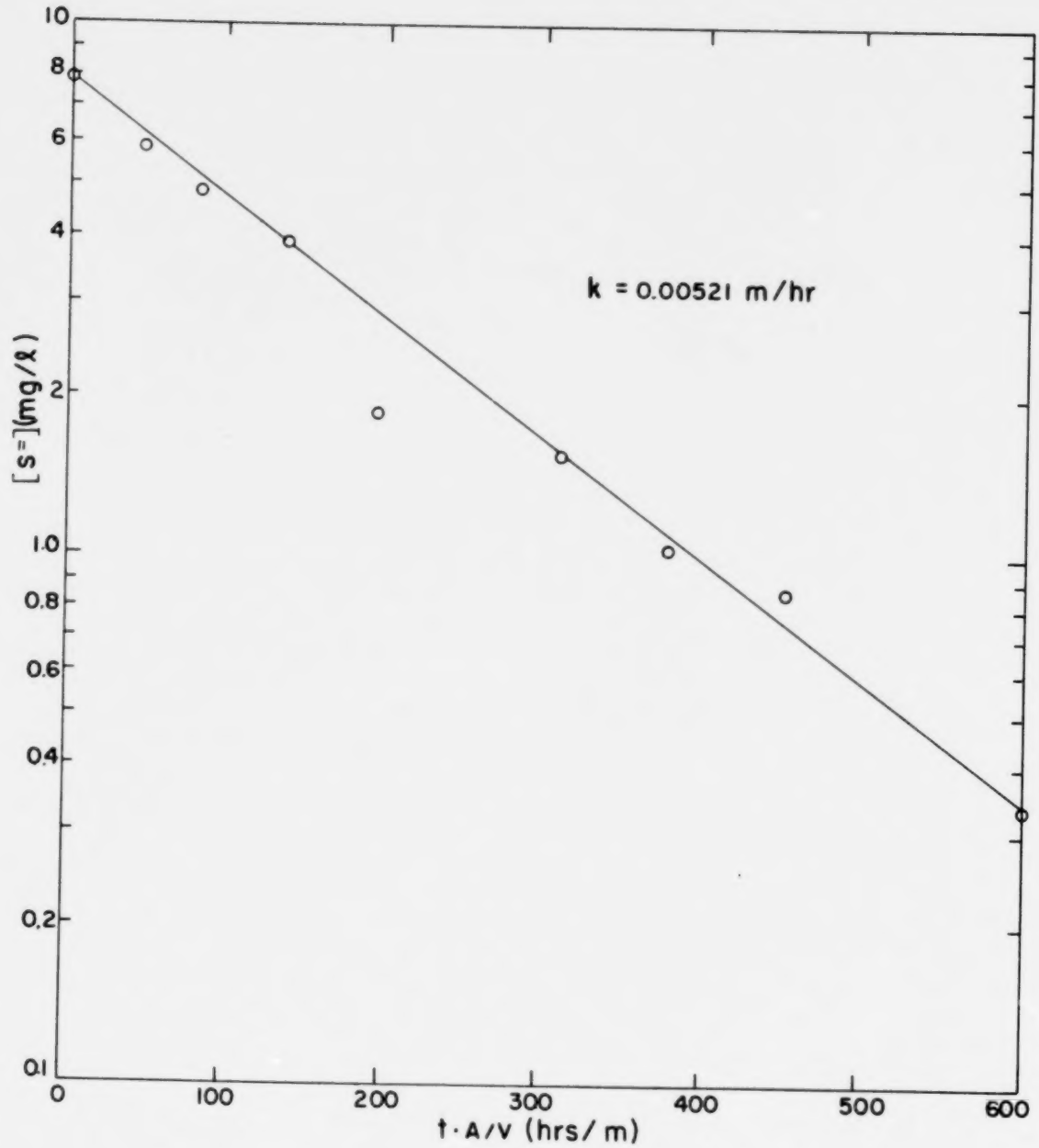



FIG. 4.38.- HYDROGEN SULFIDE TRANSFER RATE

zero the water was devoid of oxygen, so there was no sharp decrease initially in sulfide concentration. The computed k value is 0.00521 m/hr. This k value is slightly smaller than the average of tests four through seven (0.00605 m/hr). This difference was probably due to the fact that the sampling procedure used in tests four through seven resulted in more agitation in the water sample. However, generally, the results of this experiment confirm the previous explanation.

The results obtained in the qualitative analysis of gases escaping from the pond (Sections 3.3 and 4.3), where hydrogen sulfide was detected, may seem to be in disagreement with the explanation provided in this section. However, it must be kept in mind that the phenomena occurring in the pond is a dynamic process where sulfide is constantly being produced. It is quite possible that the amount of oxygen available for the oxidation of the escaping hydrogen sulfide in the surface layer of the pond water was insufficient to prevent the escape of hydrogen sulfide to the atmosphere. It should be noted that all the k values were obtained for still water. Wind effects and waves, or any other agitation, will increase the k values.

Chapter 5

# ENGINEERING DESIGN APPLICATIONS

The model pond used in this investigation is believed to simulate correctly the processes occurring in an actual pond. The model permits flexibility in the characteristics of the experiments for which it can be used. The production and release of odorous compounds from a pond can be studied in this model under controlled environmental and operating conditions. With slight modifications, the model can be used both for qualitative and quantitative analysis of gaseous emissions.

The sulfide concentration in a pond seems to be a direct function of the concentration of sulfate ion in the influent:

$$[S^{=}] = K[SO_4^{=}] \qquad (5.1)$$

An exception, of course, must be made of those wastes that may contain a high sulfide concentration. The fraction of sulfur in the influent sulfate (K), that is biochemically reduced to sulfide form, is dependent on the waste characteristics, detention time in the pond, temperature, and physical characteristics of the pond.

For a 6-foot deep facultative pond, the value of K can be estimated with the following linear relation:

$$K = a(\text{BOD surface load}) + b(\text{detention time}) + c \qquad (5.2)$$

The coefficients a, b, and c for an average pond temperature of 25°C were presented in Chapter 4. Above 15°C, the rate of biological sulfate reduction has been reported to approximately double for each 10°C rise.

For high influent sulfate concentration, two empirical linear relations were developed between sulfide concentration in the pond and BOD surface load, detention time, sulfate surface load and sulfate influent concentration. These two equations were presented and discussed in Chapter 4. Temperature considerations must also be made in the application of these two equations.

An active algal population can reduce the sulfide concentration in the upper layers of the pond to below one third of the average sulfide concentration occurring in the anaerobic part of the pond. However, increases in sulfide concentration above an average of about 7 mg/l appear to seriously inhibit photosynthetic activity. However, sulfide concentrations of 7 mg/l do not appear to affect the BOD removal efficiency. If the concentration of sulfide in the upper part of the pond does reach the sulfide concentration occurring in the bottom of the pond, odor problems will result.

Potential sulfide odor problems can be discovered in advance by continuously monitoring the ORP. Increases in sulfide concentration from zero to 1 and 2 mg/l, respectively, will cause ORP decreases of about 80 and 120 mv.

The rate of escape of hydrogen sulfide gas from the pond to the atmosphere can be expressed with Fick's diffusion equation:

$$q = k(C - C_{eq}) \qquad (5.3)$$

The rate of escape constant, k, was found to be near 0.006 m/hr under quiescent conditions at 22°C. Since the value of k is highly dependent on the rate of surface renewal, it seems desirable to undertake quantative studies of the effect of wind and waves on pond performance.

The effects of sulfide considerations on the design of a facultative pond can be illustrated with the following example:

Design Example

| | |
|---|---|
| BOD influent, 5-day, 20°C | 200 mg/l |
| BOD influent, ultimate, 20°C | 244 mg/l |
| BOD effluent, 5-day, 20°C (90% removal) | 20 mg/l |
| Quantity | 2 MGD |
| Reaction Coefficient, 35°C | 1.2 per day |
| Temperature (mean air, summer) | 30°C |
| Temperature (mean air, winter) | 20°C |
| Temperature (mean air, coldest month) | 10°C |
| Temperature coefficient | 1.085 |
| Algal toxicity factor | 1.0 |

Conventional Design

The conventional design can be made with the empirical relation developed by Gloyna (32), Eq. 4.3. The design can be based on 5-day, 20°C, BOD influent, but to compensate for a possible sludge effect, the estimates will be based on ultimate BOD, and mean air winter temperature.

$$V = C \cdot N_p \cdot q \cdot L_a^{(35-T)} \cdot f \qquad (5.4)$$

$$V = 10.7 \cdot 10^{-8} \cdot 2 \cdot 10^6 \cdot 244 \cdot 1.085^{(35-20)} \cdot 1$$

$$V = 177 \text{ Ac-ft}$$

$$\text{Depth} = 6 \text{ ft}$$

$$\text{Surface Area} = 29.5 \text{ Ac}$$

$$\text{Retention time} = \frac{177 \text{ (Ac-ft)} \cdot 325\,851 \text{ (gal/Ac-ft)}}{2 \cdot 10^6 \text{ (gal/day)}}$$

$$= 29 \text{ days}$$

$$\text{Organic load} = \frac{200 \text{ (ppm)} \cdot 2 \cdot 10^6 \text{ (gal/day)} \cdot 8.35 \text{ (lb/gal)}}{1 \times 10^6 \text{ gal}}$$

$$= 3340 \text{ lb/day}$$

$$\text{Surface organic load} = \frac{3340 \text{ lb/day}}{29.5 \text{ Ac}} = 113 \text{ lb/Ac/day}$$

Modified Design

The empirical relation developed in this investigation permits us to estimate the fraction of the influent sulfate that will be reduced in the pond to sulfide:

$$[S^{=}] = K[SO_4]$$

$$K = 0.0001185 \text{ (organic surface load)}$$

$$-0.001655 \text{ (detention time)} + 0.0553$$

$$K = 0.0001185 \cdot 113 - 0.001655 \cdot 29 + 0.0553$$

$$K = 0.0207$$

For an influent $SO_4$ concentration of 250 mg/l (as $SO_4$), the sulfide concentration that can be expected in the pond would be:

$$[S^{=}] = 0.0207 \cdot 250 = 5.18 \text{ mg/l (as S)}$$

Assuming, for the purposes of this example, an influent $SO_4$ concentration of 500 mg/l, the pond sulfide concentration would be about 10.3 mg/l. This value is above the toxic level for algae, and odor problems will occur. The design will be modified to reduce the pond sulfide concentration to 4 mg/l; then:

$$K = \frac{[S^{=}]}{[SO_4^{=}]} = \frac{4 \text{ mg/l}}{500 \text{ mg/l}} = 0.008$$

$$K = 0.008 = 0.0001185 \text{ (organic surface load)}$$
$$- 0.001655 \text{ (detention time)} + 0.0553$$

To satisfy these new design requirements several alternatives are available. One will be to keep the organic surface load constant and increase the detention time, i. e., to increase the depth of the pond. For this example the change in detention time required will be to:

$$\text{detention time} = \frac{1}{0.001655} (0.0001185 \cdot 113 + 0.0553 - 0.008)$$
$$= 37 \text{ days}$$

and the new pond depth will be 7.7'.

A second alternative will be to keep the pond depth at 6' and change both the detention time and the surface area, i.e., to change also the organic surface load. After computation, the following values were found: detention time increase from 29 to 36 days; surface area increase from 29.5 to 36.5 Ac.; and organic surface load reduce from 113 to 91 lbs/Ac/day.

# APPENDIX

TABLE 1

Substrate BOD, Starlac Concentration = 470 mg/l

| Time (days) | Test 1 (mg/l) | Test 2 (mg/l) | Test 3 (mg/l) | Test 4 (mg/l) |
|---|---|---|---|---|
| 1 | 39 | 34 | 45 | 39 |
| 2 | 183 | 188 | 198 | 190 |
| 3 | 228 | 240 | 240 | 236 |
| 4 | 277 | 280 | 288 | 281 |
| 5 | 300 | 302 | 300 | 300 |
| 10 | 330 | 345 | 340 | 338 |
| 12 | 300 | 315 | 360 | 325 |
| 15 | 366 | - | 376 | 370 |
| 20 | 395 | 410 | - | 402 |
| 25 | 360 | 525 | - | 442 |
| 27 | 630 | 480 | 320 | 480 |

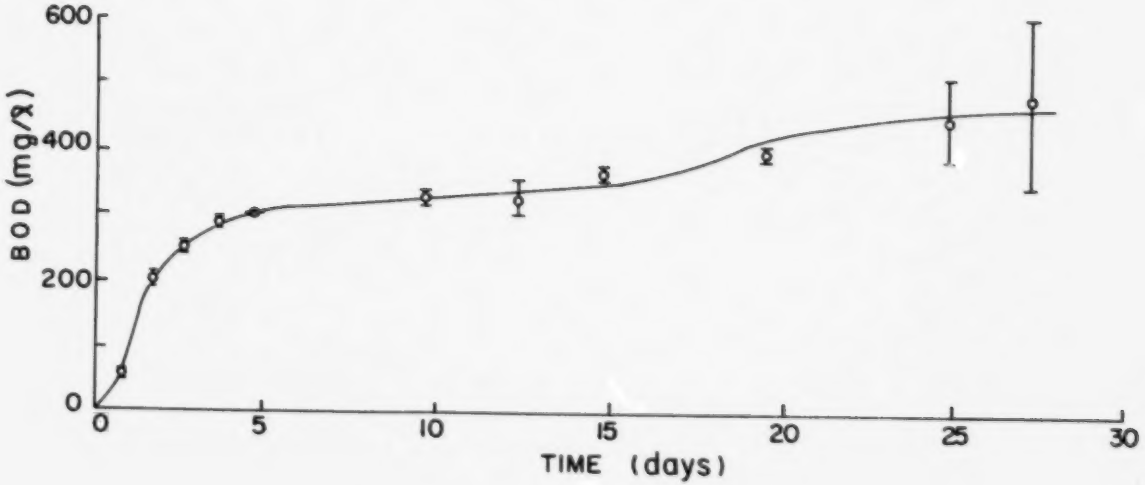



FIG. I.- LONG TERM BOD OF SUBSTRATE STARLAC
CONCENTRATION = 470 mg/ℓ

TABLE 2

Typical Dissolved Oxygen Probe Calibration Curve

| Temperature ($^{o}C$) | Temperature ($^{o}K$) | Temperature$^{-1}$ x 10000 ($1/^{o}K$) | Galvanometer Reading | Dissolved Oxygen Conc. (mg/l) | Sensitivity$^{-1}$ |
|---|---|---|---|---|---|
| 19.4 | 292.4 | 34.2 | 6.5 | 8.4 | 1.29 |
| 20.5 | 293.5 | 34.05 | 7.7 | 9.85 | 1.275 |
| 21.9 | 294.9 | 33.95 | 7.5 | 8.6 | 1.15 |
| 23.4 | 296.4 | 33.7 | 7.0 | 7.5 | 1.07 |
| 26.2 | 299.2 | 33.4 | 9.3 | 8.2 | 0.882 |

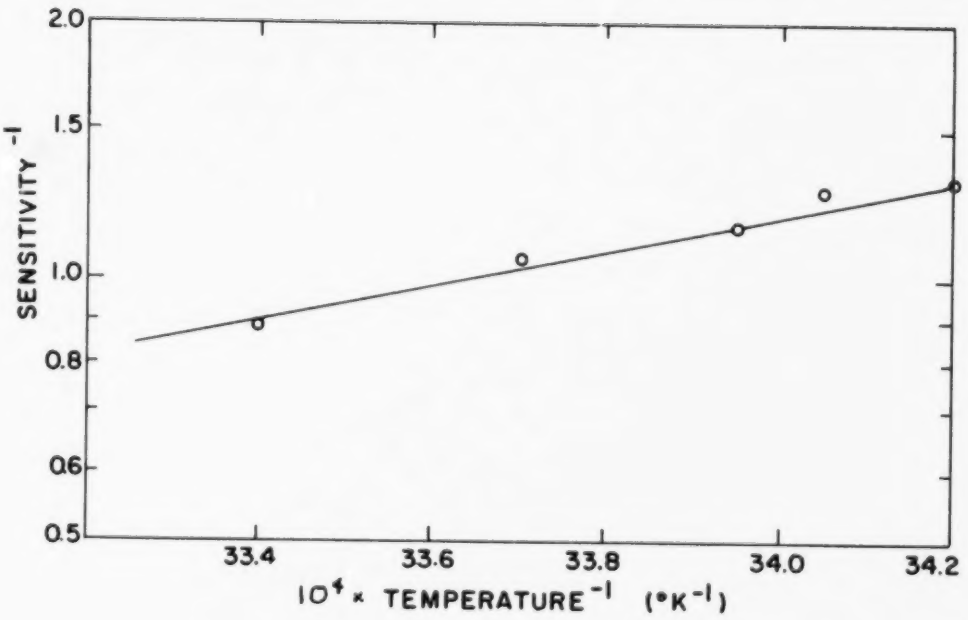



FIG. 2.- DISSOLVED OXYGEN PROBE CALIBRATION CURVE

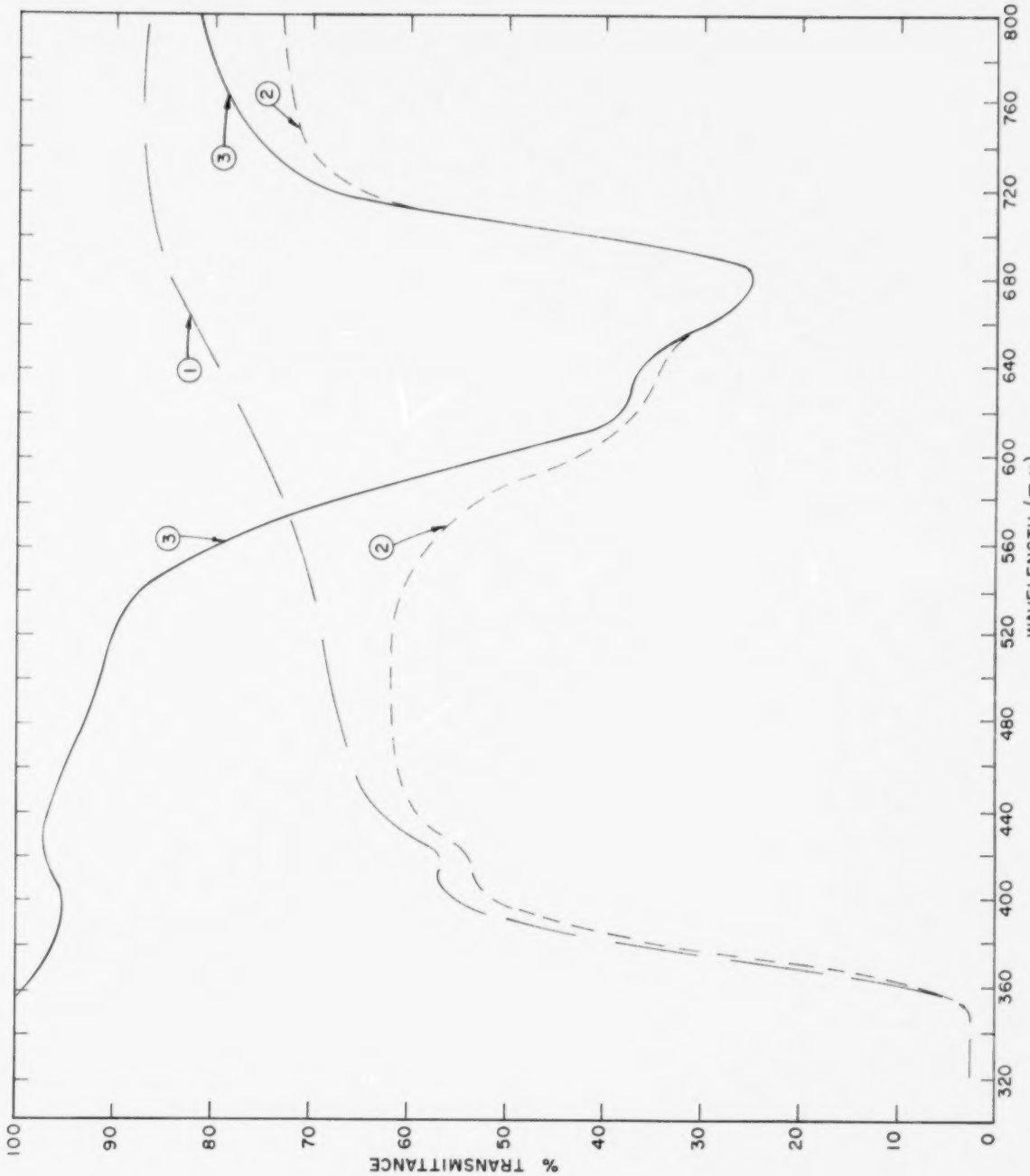



FIG. 3.- ABSORPTION SPECTRAS IN SULFIDE ANALYSIS

TABLE 3

Colorimetric Determination of Sulfide Concentration

| Transmission (%) | Concentration (mg/l) | Transmission (%) | Concentration (mg/l) | Transmission (%) | Concentration (mg/l) | Transmission (%) | Concentration (mg/l) |
|---|---|---|---|---|---|---|---|
| 96.0 | 0.12 | 66.0 | 0.58 | 37.5 | 1.06 | 22.5 | 1.75 |
| 94.5 | 0.12 | 63.0 | 0.51 | 37.5 | 1.16 | 21.5 | 1.54 |
| 93.0 | 0.13 | 60.0 | 0.46 | 36.5 | 0.96 | 21.5 | 1.83 |
| 88.5 | 0.24 | 58.5 | 0.76 | 36.5 | 1.16 | 18.5 | 1.46 |
| 87.0 | 0.26 | 57.0 | 0.59 | 36.0 | 1.00 | 18.5 | 1.50 |
| 86.0 | 0.24 | 52.5 | 0.64 | 35.5 | 1.28 | 18.5 | 1.66 |
| 84.0 | 0.19 | 52.5 | 0.90 | 35.0 | 1.28 | 17.5 | 1.80 |
| 83.0 | 0.24 | 50.5 | 0.71 | 34.5 | 1.03 | 16.5 | 1.66 |
| 82.0 | 0.26 | 50.0 | 0.76 | 32.5 | 1.03 | 15.0 | 1.91 |
| 82.0 | 0.52 | 50.0 | 0.81 | 31.5 | 1.16 | 15.0 | 2.0 |
| 80.0 | 0.36 | 47.5 | 0.74 | 31.0 | 1.41 | 14.5 | 1.84 |
| 78.5 | 0.36 | 47.0 | 0.94 | 28.0 | 1.10 | 17.0 | 2.02 |
| 78.5 | 0.39 | 47.0 | 1.00 | 27.5 | 1.44 | 12.0 | 2.21 |
| 76.0 | 0.50 | 46.5 | 0.96 | 25.5 | 1.41 | 12.0 | 2.50 |
| 73.0 | 0.39 | 40.5 | 0.78 | 24.0 | 1.29 | 10.0 | 2.20 |
| 68.0 | 0.55 | 37.5 | 1.00 | 24.0 | 1.52 | 9.0 | 3.0 |
| | | | | | | 8.8 | 2.39 |
| | | | | | | 7.5 | 2.58 |
| | | | | | | 6.5 | 2.75 |
| | | | | | | 6.3 | 2.66 |
| | | | | | | 6.3 | 3.5 |
| | | | | | | 5.5 | 3.1 |
| | | | | | | 3.0 | 3.5 |

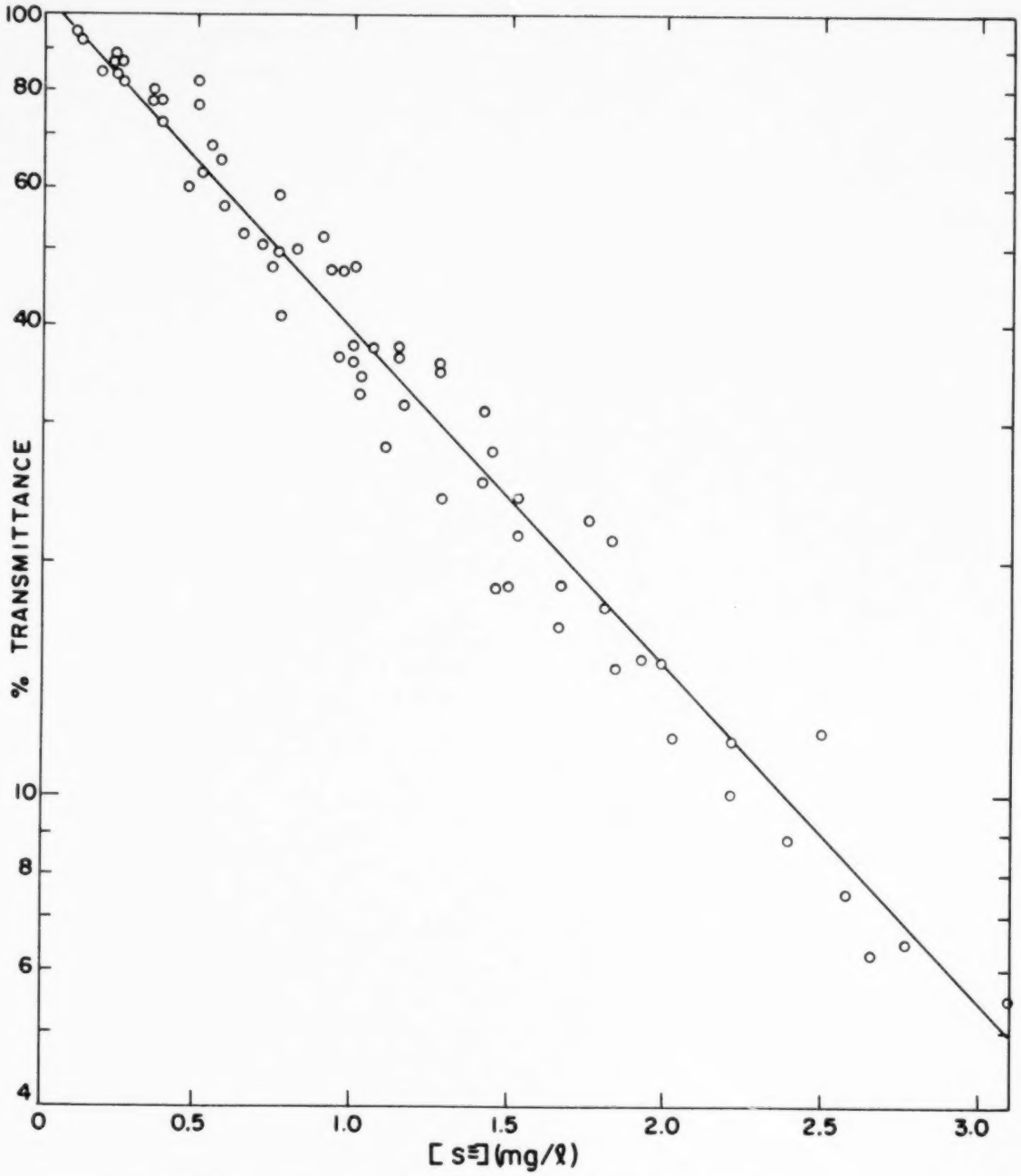



FIG. 4. - STANDARD CURVE FOR COLORIMETRIC DETERMINATION OF [S$^{=}$] CONCENTRATIONS

TABLE 4

8:00 AM Data Collected in Test No. 1 of Model Pond

| Depth (cm) | Light Intensity (ft-c) | Temperature (°C) | | | ORP (mv) | | | COD (mg/l) | | | pH | | | Sulfides as S (mg/l) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | | Average |
| Top | 800 | 23.7 | 25.2 | 24.5 | +23 | +100 | +61 | 69 | 86 | 78 | 7.2 | 7.45 | 7.22 | 0.11 | 0.15 | 0.2 | 0.15 |
| 10 | 780 | 23.4 | 25.2 | 24.3 | 0 | + 12 | 6 | 79 | 81 | 80 | 7.1 | 7.45 | 7.27 | 0.15 | 0.18 | 0.25 | 0.19 |
| 20 | 760 | 23.6 | 25.2 | 24.4 | -16 | 0 | - 8 | 69 | 70 | 70 | 7.1 | 7.45 | 7.27 | 0.15 | 0.18 | 0.23 | 0.18 |
| 30 | 720 | 23.6 | 25.2 | 24.4 | -32 | - 8 | -20 | 69 | 102 | 85 | 7.05 | 7.45 | 7.25 | - | - | - | - |
| 40 | 610 | 23.6 | 25.0 | 24.3 | -34 | - 12 | -23 | 74 | 82 | 78 | 7.0 | 7.45 | 7.22 | 0.18 | 0.37 | 0.42 | 0.32 |
| 50 | 310 | 23.6 | 25.0 | 24.3 | -44 | - 12 | -28 | 86 | 97 | 91 | 6.95 | 7.45 | 7.2 | - | - | - | - |
| 60 | 80 (At 70 cm) | 23.6 | 24.8 | 24.2 | -58 | - 16 | -37 | 73 | 90 | 81 | 6.85 | 7.45 | 7.15 | 0.35 | 0.37 | 0.70 | 0.47 |
| 80 | 0 | 23.6 | 24.8 | 24.2 | -90 | - 16 | -53 | 86 | 111 | 98 | 6.85 | 7.45 | 7.15 | 0.40 | 0.44 | 0.90 | 0.58 |
| 100 | 0 | 23.6 | 24.6 | 24.1 | -90 | - 20 | -55 | - | - | - | 6.85 | 7.45 | 7.15 | 0.42 | 0.44 | 0.75 | 0.54 |
| 120 | 0 | 23.6 | 24.6 | 24.1 | -94 | - 26 | -60 | 82 | 92 | 87 | 6.90 | 7.45 | 7.12 | 0.42 | 0.44 | 0.65 | 0.51 |
| 140 | 0 | 23.6 | 24.5 | 24.1 | - | - | - | - | - | - | - | - | - | 0.34 | 0.50 | 0.68 | 0.51 |
| 160 | 0 | 23.6 | 24.2 | 23.9 | - | - | - | 86 | - | 86 | - | - | - | 0.38 | 0.45 | 0.46 | 0.43 |

TABLE 5

8:00 PM Data Collected in Test No. 1 of Model Pond

| Depth (cm) | Temperature (°C) | | | ORP (mv) | | | COD (mg/l) | | | pH | | | Sulfides as S (mg/l) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average |
| Top | 26.2 | 30.7 | 28.5 | +220 | +224 | +222 | 58 | 72 | 65 | 7.34 | 7.64 | 7.5 | 0.0 | 0.0 | 0.0 |
| 10 | 26.1 | 30.5 | 28.3 | 210 | 212 | 211 | - | - | - | 7.35 | 7.6 | 7.5 | 0.10<br>0.07 | 0.22 | 0.13 |
| 20 | 26.0 | 29.8 | 27.9 | 200 | 204 | 202 | 61 | 69 | 65 | 7.35 | 7.6 | 7.5 | 0.22<br>0.18 | 0.24 | 0.21 |
| 30 | 25.5 | 25.7 | 25.6 | 172 | 176 | 174 | 52 | 56 | 54 | 7.0 | 7.55 | 7.25 | - | - | - |
| 40 | 25.0 | 25.2 | 25.1 | - 76 | 124 | 24 | 61<br>51 | 65 | 59 | 7.0 | 7.5 | 7.25 | 0.32 | 0.32 | 0.32 |
| 50 | 24.0 | 25.0 | 24.5 | - 78 | 10 | - 34 | 58<br>66 | 76 | 67 | 7.0 | 7.5 | 7.25 | - | - | - |
| 60 | 23.5 | 24.8 | 24.2 | - 78 | - 12 | - 45 | 52<br>62 | 66 | 60 | 7.0 | 7.2 | 7.1 | 0.17<br>0.32 | 0.42 | 0.30 |
| 80 | 23.3 | 24.7 | 24.0 | - 82 | - 16 | - 49 | 66<br>68 | 98 | 77 | 7.1 | 7.3 | 7.2 | 0.36<br>0.50 | 0.52 | 0.46 |
| 100 | 23.1 | 24.5 | 23.8 | - 55 | - 20 | - 38 | - | - | - | 6.95 | 7.3 | 7.1 | 0.36<br>0.38 | 0.58 | 0.44 |
| 120 | 23.0 | 24.3 | 23.7 | - | - | - | 68<br>71 | 75 | 71 | 7.0 | 7.3 | 7.1 | 0.44<br>0.52 | 0.54 | 0.50 |
| 140 | 23.0 | 24.2 | 23.6 | - | - | - | - | - | - | - | - | - | 0.40<br>0.44 | 0.50 | 0.45 |
| 160 | 23.0 | 24.0 | 23.5 | - | - | - | 76<br>83 | 90 | 83 | - | - | - | 0.52<br>0.72 | 0.92 | 0.72 |

TABLE 6

8:00 AM Data Collected in Test No. 2 of Model Pond

| Depth (cm) | Temperature (°C) | | | ORP (mv) | | | COD (mg/l) | pH | | | Sulfide as S (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | | Readings | | Average | |
| Top | 21.5 | 23.0 | 22.5 | +72 | +76 | +74 | 40 | 7.4 | 7.6 | 7.5 | 0.36 |
| 10 | 21.9 | 22.1 | 22.0 | 52 | 64 | 58 | 58 | 7.4 | 7.6 | 7.5 | 0.38 |
| 20 | 22.0 | 22.0 | 22.0 | 50 | 58 | 54 | 55 | 7.4 | 7.6 | 7.5 | 0.36 |
| | 21.9 | 22.0 | 22.0 | 38 | 50 | 44 | 61 | 7.4 | 7.6 | 7.5 | 0.38 |
| 40 | 21.9 | 22.0 | 22.0 | 32 | 40 | 36 | 53 | 7.4 | 7.6 | 7.5 | 0.38 |
| 50 | 21.8 | 22.0 | 21.9 | 30 | 40 | 35 | 60 | 7.4 | 7.6 | 7.5 | - |
| 60 | 21.8 | 22.0 | 21.9 | 24 | 34 | 29 | 52 | 7.4 | 7.6 | 7.5 | 0.38 |
| 80 | 21.8 | 22.0 | 21.9 | 24 | 34 | 29 | 50 | 7.4 | 7.6 | 7.5 | 0.38 |
| 100 | 21.8 | 22.0 | 21.9 | 20 | 32 | 26 | - | 7.4 | 7.5 | 7.45 | 0.45 |
| 120 | 21.8 | 22.0 | 21.9 | 16 | 28 | 22 | 49 | 7.3 | 7.4 | 7.35 | 0.75 |
| 140 | 21.8 | 22.0 | 21.9 | - | - | - | - | - | - | - | 0.94 |
| 160 | 21.8 | 22.0 | 21.9 | - | - | - | 95 | - | - | - | 0.78 |

TABLE 7

8:00 PM Data Collected in Test No. 2 of Model Pond

| Depth (cm) | Temperature (°C) | | | ORP (mv) | | | COD (mg/l) | pH | | | Sulfide as S (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | | Readings | | Average | |
| Top | 24.7 | 25.1 | 24.9 | +132 | 250 | 191 | 50 | 7.55 | 7.6 | 7.6 | 0.0 |
| 10 | 25.0 | 25.2 | 25.1 | 90 | 166 | 128 | 52 | 7.48 | 7.5 | 7.5 | 0.1 |
| 20 | 23.5 | 24.2 | 23.8 | 72 | 106 | 89 | 55 | 7.45 | 7.5 | 7.5 | 0.1 |
| 30 | 23.3 | 23.8 | 23.6 | 60 | 94 | 77 | 51 | 7.45 | 7.45 | 7.45 | - |
| 40 | 23.3 | 23.4 | 23.4 | 52 | 94 | 73 | 60 | 7.45 | 7.45 | 7.45 | 0.2 |
| 50 | 23.0 | 23.2 | 23.1 | 44 | 87 | 65 | 60 | 7.4 | 7.45 | 7.4 | - |
| 60 | 22.8 | 23.0 | 22.9 | 38 | 76 | 57 | 71 | 7.45 | 7.45 | 7.45 | 0.4 |
| 80 | 22.7 | 22.9 | 22.8 | 24 | 62 | 43 | 49 | 7.35 | 7.45 | 7.4 | 0.4 |
| 100 | 22.5 | 22.8 | 22.6 | 20 | 59 | 40 | - | 7.35 | 7.4 | 7.4 | 0.5 |
| 120 | 22.4 | 22.7 | 22.6 | 17 | 39 | 28 | 66 | 7.35 | 7.4 | 7.4 | 0.75 |
| 140 | 22.4 | 22.6 | 22.5 | - | - | - | - | - | - | - | 0.9 |
| 160 | 22.0 | 22.5 | 22.2 | - | - | - | 78 | - | - | - | 1.0 |

TABLE 8

8:00 AM Data Collected in Test No. 3 of Model Pond

| Depth (cm) | Temperature ($^{O}$C) | COD (mg/l) | | | Sulfide as S (mg/l) | | |
|---|---|---|---|---|---|---|---|
| | | Readings | | Average | Readings | | Average |
| Top | 27.6 | - | - | - | 0.1 | 0.3 | 0.2 |
| 10 | 27.8 | - | - | - | 0.3 | 0.4 | 0.35 |
| 20 | 27.6 | - | - | - | 0.8 | 1.0 | 0.9 |
| 30 | 27.5 | - | 76 | 76 | 1.2 | 1.2 | 1.2 |
| 40 | 27.2 | 48 | 72 | 60 | 1.0 | 1.0 | 1.0 |
| 50 | 27.0 | - | - | - | - | - | - |
| 60 | 26.8 | - | 64 | 64 | 1.25 | 1.3 | 1.3 |
| 80 | 26.6 | 54 | 68 | 61 | 1.1 | 1.25 | 1.2 |
| 100 | 26.5 | 52 | 79 | 65 | 1.4 | 1.6 | 1.5 |
| 120 | 26.4 | - | 102 | 102 | 1.4 | 1.4 | 1.4 |
| 140 | 26.3 | 76 | 80 | 78 | - | - | - |
| 160 | 26.2 | - | 103 | 103 | 1.5 | 1.55 | 1.5 |

TABLE 9

8:00 PM Data Collected
In Test No. 3 of Model Pond

| Depth (cm) | Temperature (°C) | Sulfide As S (mg/l) |
|---|---|---|
| Top | 38 | 0.0 |
| 10 | 34.5 | 0.7 |
| 20 | 28.8 | 0.95 |
| 30 | 28 | 1.1 |
| 40 | 27.6 | 0.75 |
| 50 | 27.5 | - |
| 60 | 27.2 | 0.9 |
| 80 | 27.0 | - |
| 100 | 26.9 | 0.9 |
| 120 | 26.8 | - |
| 140 | 26.7 | 1.15 |
| 160 | 26.6 | 1.5 |

TABLE 10

8:00 AM Data Collected in Test No. 4 of Model Pond

| Depth (cm) | Temperature (°C) | | | Dissolved Oxygen (mg/l) | | | ORP (mv) | | | pH | | | Sulfides as S (mg/l) | | | Sulfates as $SO_4$ (mg/l) | | | COD (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | |
| Top | 21.4 | 22.0 | 21.7 | 0.4 | 0.0 | 0.2 | +62 | +56 | +59 | 7.6 | 7.55 | 7.6 | 1.05 | 1.84 | 1.45 | 51.6 | 41.5 | 46.5 | 65 |
| 20 | 21.6 | 22.2 | 21.9 | 0.0 | 0.0 | 0.0 | 26 | 26 | 26 | 8.0 | 7.55 | 7.8 | 1.08 | 1.90 | 1.49 | - | - | - | - |
| 40 | 21.6 | 22.5 | 22.0 | 0.0 | 0.0 | 0.0 | -49 | 17 | -16 | 7.95 | 7.5 | 7.7 | 2.14 | 2.13 | 2.14 | 46 | 47.5 | 46.8 | 21 |
| 60 | 21.7 | 22.0 | 21.9 | 0.0 | 0.0 | 0.0 | -79 | -13 | -46 | 8.1 | 7.3 | 7.7 | 5.4 | 6.9 | 6.15 | - | - | - | - |
| 80 | 21.4 | 22.0 | 21.7 | 0.0 | 0.0 | 0.0 | -97 | -19 | -58 | 8.1 | 7.25 | 7.7 | 5.25 | 4.8 | 5.0 | 44.5 | 45.6 | 45.0 | 46 |
| 100 | 21.2 | 22.0 | 21.6 | 0.0 | 0.0 | 0.0 | -112 | -28 | -70 | 8.1 | 7.2 | 7.7 | 5.6 | 5.7 | 5.65 | - | - | - | - |
| 120 | 21.0 | 21.8 | 21.4 | 0.0 | 0.0 | 0.0 | -130 | -28 | -79 | 8.35 | 7.1 | 7.7 | 6.0 | 5.25 | 5.65 | 42 | 36 | 39 | 50 |
| 140 | 21.0 | 21.8 | 21.4 | 0.0 | 0.0 | 0.0 | -136 | -31 | -84 | 8.35 | 7.05 | 7.7 | 6.0 | 4.15 | 5.1 | - | - | - | - |
| 160 | 20.8 | 21.5 | 21.2 | 0.0 | 0.0 | 0.0 | -139 | -31 | -85 | 8.2 | 6.95 | 7.6 | 8.4 | 6.1 | 7.3 | 40.2 | 37.5 | 39 | 181 |

TABLE 11

8:00 PM Data Collected in Test No. 4 of Model Pond

| Depth (cm.) | Temperature (°C) | | | Dissolved Oxygen (mg/l) | | | ORP (mv) | | | pH | | | Sulfides as S (mg/l) | | | Sulfates as $SO_4$ (mg/l) | | | COD (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | |
| Top | 31.5 | 29 | 30.2 | 8.9 | 7.1 | 8.0 | +332 | +26 | +179 | 8.6 | 8.4 | 8.5 | 0.27 | 0.25 | 0.26 | 46.6 | 47.3 | 47.0 | 60 |
| 20 | 26.7 | 23.5 | 25.1 | 0.6 | 0.4 | 0.5 | 26 | -16 | 5 | 7.7 | 7.65 | 7.7 | 2.85 | 0.25 | 1.55 | - | - | - | - |
| 40 | 22.6 | 22.5 | 22.5 | 0.0 | 0.0 | 0.0 | - 46 | -76 | - 61 | 7.5 | 7.4 | 7.45 | 2.91 | 4.4 | 3.65 | 39 | 44.6 | 41.8 | 77 |
| 60 | 22.4 | 21.8 | 22.1 | 0.0 | 0.0 | 0.0 | - 37 | -76 | - 57 | 7.5 | 7.4 | 7.45 | 3.0 | 5.4 | 4.2 | - | - | - | - |
| 80 | 22.1 | 21.8 | 22.0 | 0.0 | 0.0 | 0.0 | - 37 | -88 | - 62 | 7.45 | 7.3 | 7.4 | 3.65 | 3.9 | 3.76 | 74 | 37.9 | 56 | 80 |
| 100 | 22.0 | 21.8 | 21.9 | 0.0 | 0.0 | 0.0 | - 52 | -91 | - 71 | 7.4 | 7.3 | 7.35 | 4.4 | 6.24 | 5.3 | - | - | - | - |
| 120 | 21.9 | 21.5 | 21.7 | 0.0 | 0.0 | 0.0 | - 58 | -97 | - 77 | 7.35 | 7.3 | 7.3 | 3.75 | 7.35 | 5.55 | 48 | 44.4 | 46.2 | 82 |
| 140 | 21.8 | 22.3 | 22.0 | 0.0 | 0.0 | 0.0 | - 61 | -97 | - 79 | 7.3 | 7.2 | 7.25 | 4.0 | 6.6 | 5.3 | - | - | - | - |
| 160 | 21.8 | 22.0 | 21.9 | 0.0 | 0.0 | 0.0 | - 61 | -97 | - 79 | 7.2 | 7.2 | 7.2 | 5.75 | 8.75 | 7.25 | 75 | 51.0 | 63 | 165 |

TABLE 12

8:00 AM Data Collected in Test No. 5 of Model Pond

| Depth (cm) | Temperature (°C) | | | Dissolved Oxygen (mg/l) | | | ORP (mv) | | | pH | | | Sulfides as S (mg/l) | | | Sulfates as $SO_4$ (mg/l) | | | COD (mg/l) | Iron as Fe (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | | |
| Top | 22.5 | 22.5 | 22.5 | 1.3 | 1.0 | 1.15 | +318 | +383 | +350 | 7.8 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 | 142 | 137 | 140 | 35 | - |
| 20 | 23.0 | 23.0 | 23.0 | 0.3 | 0.5 | 0.4 | 291 | 374 | 332 | 7.8 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 | - | - | - | - | - |
| 40 | 23.0 | 23.0 | 23.0 | 0.0 | 0.4 | 0.2 | 276 | 356 | 316 | 7.8 | 7.7 | 7.75 | 0.0 | 0.0 | 0.0 | 137 | 136 | 136 | 20 | 3.73 |
| 60 | 23.0 | 23.0 | 23.0 | 0.0 | 0.0 | 0.0 | 51 | 356 | 204 | 7.8 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 | - | - | - | - | - |
| 80 | 23.0 | 23.0 | 23.0 | 0.0 | 0.0 | 0.0 | 66 | 338 | 212 | 7.8 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 | 133 | 139 | 136 | 35 | 3.4 |
| 100 | 23.0 | 23.0 | 23.0 | 0.0 | 0.0 | 0.0 | 78 | 335 | 206 | 7.8 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 | - | - | - | - | - |
| 120 | 23.0 | 23.0 | 23.0 | 0.0 | 0.0 | 0.0 | 90 | 329 | 209 | 7.8 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 | 142 | 141 | 142 | 23 | 0.45 |
| 140 | 23.0 | 23.0 | 23.0 | 0.0 | 0.0 | 0.0 | 90 | 329 | 209 | 7.8 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 | - | - | - | - | - |
| 160 | 23.0 | 23.0 | 23.0 | 0.0 | 0.0 | 0.0 | - 24 | 74 | 25 | 7.7 | 7.5 | 7.6 | 0.0 | 0.0 | 0.0 | 129 | 148 | 138 | 20 | - |

TABLE 13

8:00 PM Data Collected in Test No. 5 of Model Pond

| Depth (cm) | Temperature (°C) | | | | Dissolved Oxygen (mg/l) | | | | Suspended Solids (mg/l) | | | COD (mg/l) | ORP (mv) | | | | pH | | | | Sulfides as S (mg/l) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | | Average | Readings | | | Average | Total | Volatile | Fixed | | Readings | | | Average | Readings | | | Average | Readings | | Average |
| Top | 26.2 | 24.2 | 23.6 | 24.7 | 2.9 | 2.4 | 1.1 | 2.1 | 18.5 | 9.5 | 9.0 | 38 | +319 | +92 | +348 | +253 | 7.7 | 7.7 | 7.7 | 7.7 | 0.0 | 0.0 | 0.0 |
| 20 | 25.4 | 24.2 | 23.6 | 24.4 | 1.2 | 1.2 | 0.6 | 1.0 | - | - | - | - | 223 | 65 | 324 | 204 | 7.7 | 7.7 | 7.7 | 7.7 | 0.0 | 0.0 | 0.0 |
| 40 | 25.0 | 24.1 | 23.5 | 24.2 | 0.8 | 1.2 | 0.6 | 0.9 | 18.5 | 10.0 | 8.5 | 40 | 225 | 53 | 324 | 201 | 7.7 | 7.7 | 7.7 | 7.7 | 0.0 | 0.0 | 0.0 |
| 60 | 24.6 | 24.1 | 23.5 | 24.1 | 0.2 | 0.5 | 0.4 | 0.4 | - | - | - | - | 225 | 47 | 330 | 201 | 7.7 | 7.7 | 7.7 | 7.7 | 0.0 | 0.0 | 0.0 |
| 80 | 24.4 | 24.1 | 23.6 | 24.1 | 0.0 | 0.0 | 0.0 | 0.0 | 17.5 | 10.0 | 7.5 | 50 | 193 | 38 | 324 | 185 | 7.7 | 7.7 | 7.6 | 7.7 | 0.0 | 0.0 | 0.0 |
| 100 | 24.2 | 24.1 | 23.6 | 24.0 | 0.0 | 0.0 | 0.0 | 0.0 | - | - | - | - | 175 | 38 | 324 | 179 | 7.7 | 7.7 | 7.7 | 7.7 | 0.0 | 0.0 | 0.0 |
| 120 | 24.2 | 24.1 | 23.6 | 24.0 | 0.0 | 0.0 | 0.0 | 0.0 | 19.5 | 12.0 | 7.5 | 38 | 187 | 27 | 319 | 174 | 7.7 | 7.7 | 7.7 | 7.7 | 0.0 | 0.0 | 0.0 |
| 140 | 24.2 | 24.1 | 23.6 | 24.0 | 0.0 | 0.0 | 0.0 | 0.0 | - | - | - | - | 193 | 27 | 324 | 181 | 7.7 | 7.7 | 7.6 | 7.7 | 0.1 | 0.0 | 0.05 |
| 160 | 24.2 | 24.1 | 23.6 | 24.0 | 0.0 | 0.0 | 0.0 | 0.0 | 17.5 | 14.0 | 3.5 | 106 | 91 | 27 | 318 | 145 | 7.7 | 7.7 | 7.6 | 7.7 | 1.15 | 2.25 | 1.1 |

TABLE 14

8:00 AM Data Collected in Test No. 6 of Model Pond

| Depth (cm) | Temperature (°C) | | | Dissolved Oxygen (mg/l) | | | ORP (mv) | | | COD (mg/l) | pH | | | Sulfide as S (mg/l) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | Readings | | Average | | Readings | | Average | Readings | | Average |
| Top | 26.4 | 26.8 | 26.6 | 2.0 | 2.7 | 2.3 | +204 | +354 | +279 | 61 | 7.85 | 7.85 | 7.85 | 0.0 | 0.0 | 0.0 |
| 20 | 25.9 | 27.2 | 26.5 | 1.8 | 2.4 | 2.1 | 177 | 348 | 257 | - | 7.85 | 7.8 | 7.8 | 0.0 | 0.77 | 0.39 |
| 40 | 25.8 | 25.4 | 25.6 | 0.7 | 1.3 | 1.0 | 36 | 0 | 18 | 32 | 7.9 | 7.9 | 7.9 | 7.3 | 7.3 | 7.3 |
| 60 | 24.3 | 24.5 | 24.4 | 0.0 | 0.6 | 0.3 | - 36 | - 39 | - 38 | - | 7.85 | 8.0 | 7.9 | 8.25 | 8.25 | 8.25 |
| 80 | 24.1 | 24.3 | 24.2 | 0.0 | 0.0 | 0.0 | - 48 | - 54 | - 51 | 28 | 7.9 | 8.0 | 7.95 | 8.25 | 8.10 | 8.2 |
| 100 | 24.0 | 23.8 | 23.9 | 0.0 | 0.0 | 0.0 | - 69 | - 62 | - 65 | - | 7.9 | 7.95 | 7.9 | 9.4 | 8.10 | 8.8 |
| 120 | 24.0 | 23.8 | 23.9 | 0.0 | 0.0 | 0.0 | - 75 | - 62 | - 69 | 28 | 7.9 | 8.05 | 8.0 | 9.0 | 8.8 | 8.9 |
| 140 | 23.9 | 23.7 | 23.8 | 0.0 | 0.0 | 0.0 | - 81 | - 87 | - 84 | - | 7.8 | 7.9 | 7.85 | 8.6 | 8.6 | 8.6 |
| 160 | 23.9 | 23.6 | 23.8 | 0.0 | 0.0 | 0.0 | - 81 | - 87 | - 84 | 25 | 7.85 | 7.9 | 7.9 | 8.2 | 8.6 | 8.4 |

TABLE 15

8:00 PM Data Collected in Test No. 6 of Model Pond

| Depth (cm) | Temperature (°C) | Dissolved Oxygen (mg/l) | ORP (mv) | COD (mg/l) | | | pH | Sulfides, as S (mg/l) | | | Suspended Solids (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Readings | | Average | | Readings | | Average | |
| Top | 37.6 | 7.8 | +368 | 26 | 51 | 38 | 8.2 | 0.0 | 0.2 | 0.1 | 33 |
| 20 | 28.5 | 0.8 | 122 | - | - | - | 8.0 | 6.3 | - | 6.3 | - |
| 40 | 25.5 | 0.3 | - 4 | 30 | 31 | 30 | 7.8 | 5.0 | 9.1 | 7.0 | 9 |
| 60 | 25.5 | 0.0 | - 25 | - | - | - | 7.75 | 5.0 | - | 5.0 | - |
| 80 | 25.0 | 0.0 | - 52 | 28 | 25 | 26 | 7.75 | 6.0 | 10.6 | 8.3 | 7 |
| 100 | 25.0 | 0.0 | - 73 | - | - | - | 7.8 | 6.65 | - | 6.65 | - |
| 120 | 25.0 | 0.0 | - 73 | 26 | 25 | 26 | 7.8 | 6.5 | 9.5 | 8.0 | 7 |
| 140 | 24.9 | 0.0 | - 73 | - | - | - | 7.8 | 7.4 | - | 7.4 | - |
| 160 | 24.0 | 0.0 | - | 28 | 33 | 30 | 7.7 | 8.45 | 5.8 | 7.15 | 7 |

TABLE 16

8:00 AM Data Collected in Test No. 7 of Model Pond

| Depth (cm) | Temperature (°C) | | | Dissolved Oxygen (mg/l) | | | ORP (mv) | | | pH | | | COD (mg/l) | | | Sulfides as S (mg/l) | | | Sulfates as $SO_4$ (mg/l) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average |
| Top | 24.7 | 25.0 | 24.85 | 0.0 | 0.0 | 0.0 | - 40 | - 34 | - 37 | 7.3 | 7.3 | 7.3 | 61 | 46 | 53 | 9.0 | - | 9.0 | 208 | 205 | 206 |
| 20 | 25.0 | 25.1 | 25.05 | 0.0 | 0.0 | 0.0 | - 82 | -112 | - 97 | 7.4 | 7.3 | 7.35 | - | - | - | 7.5 | - | 7.5 | - | - | - |
| 40 | 25.0 | 25.1 | 25.05 | 0.0 | 0.0 | 0.0 | -136 | -154 | -145 | 7.3 | 7.3 | 7.3 | 31 | - | 31 | 8.5 | 8.2 | 8.36 | 210 | 211 | 210 |
| 60 | 25.0 | 25.1 | 25.05 | 0.0 | 0.0 | 0.0 | -142 | -214 | -178 | 7.3 | 7.3 | 7.3 | - | - | - | 9.6 | - | 9.6 | - | - | - |
| 80 | 25.0 | 25.1 | 25.05 | 0.0 | 0.0 | 0.0 | -136 | -202 | -169 | 7.25 | 7.3 | 7.3 | 34 | 33 | 33 | 9.1 | - | 9.1 | 205 | 205 | 205 |
| 100 | 25.0 | 25.1 | 25.05 | 0.0 | 0.0 | 0.0 | -136 | -196 | -166 | 7.25 | 7.3 | 7.3 | - | - | - | 9.4 | - | 9.4 | - | - | - |
| 120 | 25.0 | 25.1 | 25.05 | 0.0 | 0.0 | 0.0 | -136 | -188 | -162 | 7.2 | 7.3 | 7.25 | 34 | 38 | 36 | 10.3 | 9.7 | 10.0 | 210 | - | 210 |
| 140 | 24.9 | 25.1 | 25.0 | 0.0 | 0.0 | 0.0 | -136 | -190 | -163 | 7.25 | 7.3 | 7.3 | - | - | - | 10.3 | 8.8 | 9.55 | - | - | - |
| 160 | 24.9 | 25.1 | 25.0 | 0.0 | 0.0 | 0.0 | -136 | -184 | -160 | 7.2 | 7.3 | 7.25 | 33 | 44 | 38 | 10.7 | 9.0 | 9.85 | 207 | 208 | 207 |

TABLE 17

8:00 PM Data Collected in Test No. 7 of Model Pond

| Depth (cm) | Temperature (°C) | | | Dissolved Oxygen (mg/l) | | | ORP (mv) | | | pH | | | Sulfides as S (mg/l) | | | Suspended Solids (mg/l) | | | Sulfates as $SO_4$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Readings | | Average | Total | Volatile | Fixed | |
| Top | 30.5 | 31.4 | 31.0 | 0.0 | 0.0 | 0.0 | - 30 | +11 | -10 | 7.35 | 7.55 | 7.45 | 0.1 | 1.2 | 0.65 | 16.0 | 16.0 | 0.0 | 205 |
| 20 | 28.5 | 27.4 | 28.0 | 0.0 | 0.0 | 0.0 | - 54 | -25 | -40 | 7.2 | 7.5 | 7.35 | 4.0 | 4.8 | 4.4 | - | - | - | - |
| 40 | 28.0 | 27.4 | 27.7 | 0.0 | 0.0 | 0.0 | - 84 | -46 | -65 | 7.2 | 7.45 | 7.3 | 7.0 | 7.75 | 7.4 | 15.0 | 15.0 | 0.0 | 211 |
| 60 | 27.8 | 27.4 | 27.6 | 0.0 | 0.0 | 0.0 | - 87 | -52 | -70 | 7.2 | 7.45 | 7.3 | 8.3 | 9.15 | 8.7 | - | - | - | - |
| 80 | 27.6 | 27.1 | 27.3 | 0.0 | 0.0 | 0.0 | -106 | -67 | -86 | 7.2 | 7.45 | 7.3 | 9.7 | 11.6 | 10.65 | 16.0 | 16.0 | 0.0 | 205 |
| 100 | 27.6 | 27.0 | 27.3 | 0.0 | 0.0 | 0.0 | -106 | -73 | -90 | 7.2 | 7.45 | 7.3 | 9.5 | 11.6 | 10.55 | - | - | - | - |
| 120 | 27.6 | 26.8 | 27.2 | 0.0 | 0.0 | 0.0 | -106 | -73 | -90 | 7.1 | 7.45 | 7.3 | 9.7 | 10.6 | 10.65 | 15.0 | 15.0 | 0.0 | - |
| 140 | 27.2 | 26.7 | 27.0 | 0.0 | 0.0 | 0.0 | -106 | -73 | -90 | 7.1 | 7.45 | 7.3 | 10.8 | 11.6 | 11.0 | - | - | - | - |
| 160 | 27.2 | 26.7 | 27.0 | 0.0 | 0.0 | 0.0 | -106 | -73 | -90 | 7.0 | 7.4 | 7.2 | 9.8 | 10.9 | 10.4 | 14.0 | 14.0 | 0.0 | 208 |

TABLE 18

Sulfide Concentrations in Tests 1, 2 and 3

| Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | Test 1 Total $[S^{=}]$ (mg/l) | Test 1 Average $[H_2S]$ (mg/l) | Test 2 Total $[S^{=}]$ (mg/l) | Test 2 Average $[H_2S]$ (mg/l) | Test 3 Total $[S^{=}]$ (mg/l) | Test 3 Average $[H_2S]$ (mg/l) |
|---|---|---|---|---|---|---|---|
| 0:00 | 0.0 | 7.1<br>7.1 | 3.4 | 9.5<br>12.0 | 5.15 | 7.5<br>7.65 | 0.96 |
| 0:15 | 1.37 | 6.0<br>7.25 | 3.15 | - | - | 5.05<br>6.7 | 0.75 |
| 0:30 | 2.75 | 6.15<br>- | 2.45 | 6.0<br>7.61 | 3.25 | 5.8<br>7.3 | 0.82 |
| 1:00 | 5.5 | -<br>- | - | 5.08<br>- | 2.47 | -<br>- | - |
| 1:30 | 8.25 | 3.35<br>- | 1.6 | 4.7<br>4.5 | 2.2 | 3.95<br>4.9 | 0.56 |
| 2:00 | 11.0 | -<br>- | - | 4.6<br>6.51 | 2.65 | -<br>- | - |
| 2:30 | 13.75 | 2.8<br>4.12 | 1.65 | -<br>- | - | 2.76<br>4.1 | 0.43 |
| 3:00 | 16.5 | -<br>- | - | 4.7<br>6.02 | 2.55 | -<br>- | - |
| 3:45 | 20.62 | 2.62<br>3.45 | 1.45 | -<br>- | - | 1.12<br>1.5 | 0.165 |
| 4:00 | 22.0 | -<br>- | - | 3.56<br>5.02 | 2.05 | -<br>- | - |
| 5:00 | 27.5 | -<br>- | - | 3.14<br>3.94 | 1.68 | -<br>- | - |
| 7:00 | 38.5 | -<br>- | - | 1.59<br>2.55 | 1.00 | -<br>- | - |
| 10:30 | 57.75 | -<br>- | - | 0.18<br>0.30 | 0.11 | -<br>- | - |
| 18:30 | 101.75 | 0.15<br>0.15 | 0.072 | -<br>- | - | -<br>- | - |

TABLE 19

Sulfide Concentrations in Tests 4 and 5

| Test 4 | | | Test 5 | | |
|---|---|---|---|---|---|
| Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | $[S^{=}]$ (mg/l) | Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | $[S^{=}]$ (mg/l) |
| 0:00 | 0.00 | 13.8<br>15.3 | 0:00 | 0 | 19.0<br>19.6 |
| 0:36 | 3.3 | 15.0<br>15.3 | 0:36 | 5 | 16.5<br>17.7 |
| 1:12 | 6.6 | 12.9<br>15.3 | 1:12 | 10 | 18.1<br>18.4 |
| 1:48 | 9.9 | 13.5<br>13.8 | 1:48 | 15 | 16.8<br>18.3 |
| 2:24 | 13.2 | -<br>- | 2:24 | 20 | -<br>- |
| 3:01 | 16.5 | 10.9<br>12.3 | 3:01 | 25 | 12.3<br>12.4 |
| 3:36 | 19.8 | 9.8<br>10.9 | 3:36 | 30 | 10.9<br>11.3 |
| 4:50 | 26.5 | 8.25<br>11.25 | 4:50 | 40 | 10.6<br>12.4 |
| 7:51 | 43.2 | 7.45<br>9.00 | 7:51 | 65 | 7.5<br>8.4 |
| 11:20 | 62.4 | 7.50<br>7.85 | 11:20 | 94 | 7.4<br>9.5 |
| 48:00 | 264 | 1.87<br>2.03 | 48:00 | 395 | 1.1<br>1.2 |
| 48:00 | 264 | 1.68<br>1.74 | 48:00 | 395 | 1.16<br>1.21 |
| 71:30 | 393 | 0.82<br>0.90 | 71:30 | 590 | 0.34<br>0.4 |

TABLE 20

Sulfide Concentrations in Tests 6 and 7

| Test 6 | | | Test 7 | | |
|---|---|---|---|---|---|
| Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | $[S^{=}]$ (mg/l) | Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | $[S^{=}]$ (mg/l) |
| 0:00 | 0 | 6.15<br>7.50 | 0:00 | 0 | 1.27<br>2.25 |
| 3:00 | 16.5 | 6.0<br>7.05 | 3:00 | 25 | 1.35<br>1.12 |
| 6:00 | 33 | 5.4<br>6.3 | 6:00 | 50 | 1.43<br>1.05 |
| 12:00 | 66 | 4.4<br>4.3 | 7:00 | 58 | 0.83<br>0.84 |
| - | - | -<br>- | 12:00 | 100 | 0.43<br>0.45 |
| 25:30 | 139 | 2.4<br>2.4 | 25:30 | 211 | 0.22<br>0.22 |
| 30:00 | 165 | 1.6<br>2.0 | 30:00 | 247 | 0.20<br>0.20 |
| 37:45 | 206 | 1.65<br>1.65 | 37.45 | 309 | 0.16<br>0.16 |
| 48:00 | 264 | 1.1<br>1.1 | 48:00 | 397 | -<br>- |
| 54:00 | 297 | 0.9<br>0.8 | 54:00 | 446 | -<br>- |
| 72:00 | 395 | 0.4<br>0.5 | 72:00 | 594 | -<br>- |
| 84:00 | 462 | 0.3<br>0.3 | 84:00 | 694 | -<br>- |
| 96:00 | 528 | 0.18<br>0.18 | 96:00 | 794 | -<br>- |

TABLE 21

Sulfide Concentrations in Tests 8, 9 and 10

| Test 8 | | | Test 9 | | | Test 10 | | |
|---|---|---|---|---|---|---|---|---|
| Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | $[S^{=}]$ (mg/l) | Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | $[S^{=}]$ (mg/l) | Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | $[S^{=}]$ (mg/l) |
| 0:00 | 0 | 27<br>30.8 | 0:00 | 0 | 17.9<br>20.8 | 0:00 | 0 | -<br>31.8 |
| 3:00 | 16.5 | 23.1<br>27 | 3:00 | 25 | 15.9<br>19.6 | 3:00 | 50 | -<br>24.6 |
| 6:00 | 33 | 20.6<br>23.2 | 6:00 | 50 | 13.1<br>13.8 | 6:00 | 100 | 13.9<br>13.7 |
| 12:00 | 66 | 16.6<br>16.0 | 12:00 | 100 | 8.8<br>9.2 | 12:00 | 200 | 8.2<br>8.2 |
| 25:30 | 140 | 9.56<br>10.2 | 25:30 | 210 | 4.5<br>4.8 | 25:30 | 420 | 1.71<br>- |
| 30:00 | 165 | 7.64<br>8.64 | 30:00 | 248 | 3.6<br>3.6 | 30:00 | 496 | 1.2<br>1.15 |
| 37:45 | 208 | 6.30<br>6.75 | 37:45 | 309 | 2.7<br>2.25 | 37:45 | 618 | 0.57<br>0.50 |
| 48:00 | 264 | 4.5<br>4.57 | 48:00 | 397 | 1.35<br>1.56 | 48:00 | 794 | 0.24<br>0.17 |
| 54:00 | 297 | 3.90<br>4.27 | 54:00 | 446 | 0.93<br>1.14 | 54:00 | 892 | 0.13<br>0.11 |
| 72:00 | 396 | 1.96<br>2.40 | 72:00 | 595 | 0.30<br>0.30 | - | - | -<br>- |
| 84:00 | 462 | 1.0<br>1.1 | 84:00 | 694 | 0.12<br>0.13 | - | - | -<br>- |
| 96:00 | 528 | 0.7<br>0.7 | 96:00 | 793 | 0.10<br>0.10 | - | - | -<br>- |

TABLE 22

Oxygen Diffusion Results

| | Test 11 V = 3l | | | Test 12 V = 2l | | |
|---|---|---|---|---|---|---|
| Time (hrs:min) | $t \cdot \frac{A}{V}$ (hrs/m) | C (mg/l) | $C_s - C$ (mg/l) | $t \cdot \frac{A}{V}$ (hrs/m) | C (mg/l) | $C_s - C$ (mg/l) |
| 0:00 | 0 | 0.25 | 8.5 | 0 | 0.3 | 8.45 |
| 10:45 | 57 | 2.85 | 5.9 | 86 | 4.4 | 4.35 |
| 14:30 | 77 | 3.5 | 5.25 | 115 | 5.75 | 3.00 |
| 21:45 | 116 | 4.8 | 3.95 | 172 | 6.35 | 2.40 |
| 35:45 | 184 | 6.1 | 2.65 | 286 | 7.15 | 1.60 |
| 64:00 | 339 | 7.35 | 1.4 | 511 | 7.95 | 0.8 |

TABLE 23

Sulfide Concentrations in Test 13

| Time (hr:min) | $t \cdot \frac{A}{V}$ (hrs/m) | Average $[S^{=}]$ (mg/l) |
|---|---|---|
| 0 | 0 | 7.8 |
| 8:00 | 50 | 5.7 |
| 13:30 | 84.5 | 4.7 |
| 23:00 | 144 | 3.8 |
| 31:30 | 197 | 1.83 |
| 49:00 | 306 | 1.52 |
| 61:00 | 381 | 1.02 |
| 73:00 | 456 | 0.87 |
| 97:30 | 610 | 0.33 |

BIBLIOGRAPHY


1. Aguirre, J., and E. F. Gloyna, "Nitrification and Denitrification in a Model Waste Stabilization Pond", Center for Research in Water Resources, The University of Texas, Austin, Texas, 1967.

2. Aleshina, W. L., "Decomposition of Chitin by Sulfate Reducing Bacteria and Changes in Oxidation-Reduction Conditions During the Process of Reduction of Sulfates", Microbiology, Moscow, Z, 850, 1938, quoted by Wheatland (73).

3. Bates, R. G., Determination of pH, Theory and Practice, John Wiley and Sons, Inc., New York, N. Y., 1964.

4. Bennett, C. O., and J. E. Myers, Momentum, Heat and Mass Transfer, McGraw Hill Book Co., Inc., New York, N. Y., 1962.

5. Bolton, E. T., D. B. Cowie, and M. K. Sands, "Sulfur Metabolism in Escherichia Coli", Journal of Bacteriology, 63, 309, 1952.

6. Boyer, P. D., H. Lardy and K. Myrback, The Enzymes, Academic Press, New York, 1960.

7. Brasted, R. C., Comprehensive Inorganic Chemistry, Vol. VIII, D. Van Nostrand Co., Inc., New York, N. Y., 1961.

8. Bunker, H. J., "A Review of the Physiology and Biochemistry of the Sulfur Bacteria," His Majesty Stationery Office, London, England, 1936.

9. Butlin, K. R., S. C. Selwyn, and D. S. Wakerley, "Sulfide Production from Sulfate Enriched Sewage," Journal of Applied Bacteriology, 19, 1, 3, 1956.

10. Camp, T. R., Water and Its Impurities, Reinhold Publishing Corp. New York, N. Y., 1963.

11. Clare, H. C., J. K. Neel, and C. A. Monday, Jr., "Studies of Raw Sewage Lagoons at Fayette, Missouri, 1958-59 with a Resume of 1957-58 Operations", Proc. Symposium on Waste

Stabilization Lagoons", Water Supply and Pollution Control Activities, Region VI, U.S. Public Health Service, 1960.

12. Coetzee, O. J., and N. A. Fourie, "The Efficiency of Conventional Sewage Purification Works, Stabilization Ponds and Maturation Ponds with Respect to the Survival of Pathogenic Bacteria and Indicator Organisms", Journal of the Inst. of Sewage Purification, London, England, 3, 210, 1965.

13. Conn, E. E., and P. K. Stumpf, Outlines of Biochemistry, John Wiley and Sons, Inc., New York, 1963.

14. Cooper, R. C., "Photosynthetic Bacteria in Waste Treatment," Developments on Industrial Microbiology, 4, 95, 1963.

15. _____, "Drinking Water Standards", Publication No. 956, Public Health Service, U.S. Department of Health, Education, and Welfare, Washington, D. C., 1962.

16. Drynan, W. R., and E. F. Gloyna, "Oxidation-Reduction Potential Measurements in Waste Treatment Systems", South West Water Works Journal, p. 28, June, 1959.

17. Gloyna, E. F., "Waste Stabilization Pond Design", Environmental Engineering Conference, American Society of Civil Engineers, Dallas, Texas, February, 1967.

18. Green, R. H., "Activities of Purple Sulfur Bacteria in Waste Stabilization Ponds", Ph.D. Dissertation, Washington State University, Seattle, Washington, 1966.

19. Gregory, J. D., and P. W. Robbins, "Metabolism of Sulfur Compounds," Annual Review of Biochemistry, 29, 347, 1960.

20. _____, Handbook of Physics and Chemistry, 38th Edition, The Chemical Rubber Co., 1956-57.

21. Hermann, E. R., "Stabilization Pond as Nitrate Reducing Reactor", Journal Sanitary Engineering Division, American Society of Civil Engineers, 88, SA5, 1962.

22. Hermann, E. R., and E. F. Gloyna, "Development of Design Criteria for Waste Stabilization Ponds", Report to Atomic Energy Commission, Civil Engineering Dept., The University of Texas, Austin, Texas, March, 1957.

23. Heukelekian, H., "Effect of the Addition of $NaNO_3$ to Sewage on Hydrogen Sulfide Production and BOD Reduction", Sewage Works Journal, 15, 2, 256, 1943.

24. Hewitt, L., Oxidation-Reduction Potentials in Bacteriology and Biochemistry, 6th Ed., E and S Livingstone Ltd., Edinburgh, England, 1950.

25. Higgins, P. M. "Waste Stabilization Ponds-Health Hazard or Effective Treatment Device", Canadian Municipal Utilities, 103, 2 35, 1965.

26. Huang, J. C., and E. F. Gloyna, "Effects of Organics on Photosynthetic Reoxygenation", Technical Report, Center for Research in Water Resources, The University of Texas, Austin, Texas, August, 1967.

27. Hutchinson, G. E., A Treatise on Limnology, Vol. I, John Wiley and Sons, Inc., New York, 1957.

28. Ippen, A. T., and C. E. Carver, "Technical Report No. 14", Hydrodynamics Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, April, 1955.

29. Ippen, A. T., L. G. Campbell, and C. E. Carver, "Technical Report No. 7", Hydrodynamics Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, May, 1952.

30. Johnson, N. L., and F. C. Leone, Statistics and Experimental Design, Vol, II, John Wiley and Sons, Inc., New York, N. Y., 1964.

31. Kott, Y., G. Hershkowitz, A. Shemtob, and J. B. Sless, "Algicidal Effects of Bromine and Chlorine on Chlorella Pyrenoidosa", Appl. Microbiology, 14, 1, 8, 1966.

32. Lackey, J. B., E. W. Lackey and G. B. Morgan, "Taxonomy and Ecology of the Sulfur Bacteria", Engineering Progress at the University of Florida, XIX, 3, 1965.

33. Lewin, R., Ed., Physiology and Biochemistry of Algae, Academic Press, New York, 1962.

34. Lewis, R. F., "Control of Sulfate-Reducing Bacteria", Journal American Water Works Association, 57, 8, 1965.

35. Lindstrom, E. S., "Ecology and Physiology of the Photosynthetic Bacteria", in Heukelekian, H., and N. C. Pondero (Ed), Principles and Application in Aquatic Microbiology, John Wiley and Sons, Inc., New York, 1964.

36. Mahlie, W. S., "Removal of $H_2S$ in Sewage by Aeration," Sewage Works Journal, 7, 1, 91, 1935.

37. Mancy, K. H., and W. C. Westgarth, "A Galvanic Cell Oxygen Analyzer", Journal Water Pollution Control Federation, 34, 10, 1037, 1962.

38. Marais, G. v. R., "New Factors in the Design, Operation and Performance of Waste-Stabilization Ponds", Bulletin of the World Health Organization, 34, 737, Geneva, Switzerland, 1966.

39. Marais, G. v. R., and A. J. Beer, "Measurement of Dissolved Oxygen Concentration in Oxidation Ponds", Publication No. 136, School of Public Health, University of North Carolina Chapel Hill, N. C., 1966.

40. Marais, G. v. R., and V. A. Shaw, "A Rational Theory for Design of Sewage Oxidation Ponds, in Central and South Africa", Trans. South African Inst. Civ. Eng., 3, 205, 1961.

41. McAnulty, J., "Sleepy Lagoons", Journal of the Canadian Medical Association, 19, 1964, November, 1964.

42. McKinney, P. E., Microbiology for Sanitary Engineers, McGraw Hill Co., Inc., New York, 1962.

43. Nelson, R. Y., and J. O. Ledbetter, "Atmosphere Emissions from Oxidation Ponds", Journal of the Air Pollution Control Association, 14, 2, 50, 1964.

44. Nemerov, N. L., Theories and Practices of Industrial Waste Treatment, Addision-Wesley Publishing Co., Reading, Massachusetts, 1963.

45. Noller, C. R., "Textbook of Organic Chemistry", W. B. Saunders Co., Philadelphia, Pennsylvania, 1958.

46. O'Connor, E. J., and W. E. Dobbins, "The Mechanism of Reaeration in Natural Streams", Transactions American Society of Civil Engineers, 123, 641, 1958.

47. Ohle, W., "Die Ursachen der Rasanten Seeneutrophierung" Verh. Int. Ver. Limnol., 11, 3 3, 1955, quoted by Hutchinson (14).

48. Oswald, W. J., "Rational Design of Waste Ponds", Proc. of Symposium on Waste Treatment by Oxidation Ponds, Nagpur, India, Central Public Health Engr. Research Institute, 1964.

49. Oswald, W. J., "Advances in Anaerobic Pond Systems Design", Special Lecture Series on Advances in Water Quality Improvement, The University of Texas, Austin, Texas, April, 1966.

50. Palmer, C. M., "Algae in Water Supplies", Publication No. 657, Public Health Service, U. S. Department of Health, Education, and Welfare, Washington, D. C., 1962.

51. Parker, C. D., "Microbiological Aspects of Lagoon Treatment", Journal of the Water Pollution Control Federation, 34, 149, 1962.

52. Parker, C. D., H. L. Jones, and N. C. Greene, "Performances of Large Sewage Lagoons at Melbourne, Australia", Sewage and Industrial Wastes, 31, 133, 1959.

53. Peck, H. D., "The ATP-Dependent Reduction of Sulfate with Hydrogen in Extracts of Desulfovibrio Desulfuricans", Proc. National Academy of Sciences, 45, 70', 1959.

54. Perry, J. H. (Ed.), Chemical Engineering Handbook, McGraw Hill Book Co., Inc., New York, N. Y., 1950.

55. Pierson, R. H., A. N. Fletcher, and E. St. Clair Gantz, "Catalog of Infrared Spectra for Qualitative Analysis of Gases", Analytical Chemistry, 28, 8, 1231, August, 1956.

56. Porger, R., and K. M. Mackenthun, "Waste Stabilization Ponds; the Function and Biota", Biotechnology and Bioengineering, V, 255, 1963.

57. Reid, R. C. and T. K. Sherwood, The Properties of Gases and Liquids, McGraw Hill Book Co., Inc., New York, N. Y., 1958.

58. Ruttner, F., Fundamentals of Limnology, University of Toronto Press, Toronto, Canada, 1953.

59. Sawyer, C. N., Chemistry for Sanitary Engineers, McGraw Hill Co., Inc., New York, 1960.

60. Schiff, J. A., "Preliminary Studies on the Sulfur Metabolism of Chlorella Pyrenoidosa with Sulfur-35", Ph.D. Thesis, University of Pennsylvania, Abstract No. 17271, American Abstracts, 1956.

61. Schiff, J. A., "Studies on Sulfate Utilization by Chlorella Pyrenoidosa", Plant Physiology, 34, 73, 1959.

62. Silva, P. C., and G. F. Papenfuss, "A Systematic Study of the Algae of Sewage Oxidation Ponds", California Water Pollution Control Board Publication No. 7, Sacramento, California, 1953.

63. Silverstein, R. M., and G. C. Bassler, Spectrometric Identification of Organic Compounds, John Wiley and Sons, Inc., New York, New York, 1964.

64. _____, Standard Methods for the Examination of Water and Wastewater, 12th Ed., American Public Health Association, Inc., New York, New York, 1965.

65. Stanier, R. Y., M. Doudoroff, and E. A. Adelberg, The Microbial World, 2nd Edition, Prentice Hall, Inc., 1962.

66. Suwannakarn, V., "Temperature Effects on Waste Stabilization Pond Treatment", Ph.D. Thesis, The University of Texas, Austin, Texas, 1963.

67. _____, "The Beckman Pneumatic Air Dryer", Bulletin 7000-6, Scientific and Process Instruments Division, Beckman Instruments, Inc., Fullerton, California.

68. Thimann, K. V., The Life of Bacteria, The MacMillan Co., New York, New York, 1963.

69. Thirumurthi, D., and E. F. Gloyna, "Relative Toxicity of Organics to Chlorella Pyrenoidosa" Technical Report, Center for Research in Water Resources, The University of Texas, Austin, Texas, November, 1965.

70. _____, "Threshold Limit Values", Industrial Hygiene, Occupational Health Bulletin, 13, Texas State Department of Health Austin, Texas, January, 1967.

71. _____, "Tracking Down Trace Impurities", The Analyzer, Published by the Scientific and Process Instruments Division, Beckman Instruments, Inc., Fullerton, California, May, 1967.

72. Wedding, R. T. and M. K. Black, "Uptake and Metabolism of Sulfate by Chlorella", Plant Physiology, 35, 72, 1960.

73. Wheatland, A. B., "Factors Affecting the Formation and Oxidation of Sulfides in a Polluted Estuary", The Journal of Hygiene, London, England, 52, 194, 1954.

74. Young, L. and G. A. Maw, The Metabolism of Sulfur Compounds Methuen and Co., Ltd., London, 1958.

75. Zo Bell, C. E., and S. C. Rittenberg, "Sulfate Reducing Bacteria in Marine Sediments", Journal of Marine Research, London, England, 52, 194, 1954.